REPORT

RECOMMENDATIONS ON THE DEVELOPMENT OF CHEMICAL SENSORS AND FIELD DEPLOYABLE INSTRUMENTATION FOR DOE NEEDS

CHAPTER 1

INTRODUCTION

The Office of Science and Technology (OST) of the Environmental Management (EM) division of the Department of Energy (DOE) is promoting the use of new technologies to accomplish waste cleanup and environmental remediation more cost effectively and more rapidly at DOE sites. The mission of the Characterization, Monitoring, and Sensor Crosscutting Program (CMST-CP), within OST (EM-50), is to provide needed technology solutions for characterization of waste and of site contamination as well as for monitoring processes such as waste destruction, environmental restoration, pollution control, and containment of contaminants.

To aid technology development efforts, the technical field support office for CMST-CP at Ames Laboratory, Ames, IA has undertaken efforts to better define the environmental characterization and monitoring needs of both the DOE and commercial markets, document what technologies are now available to meet these needs, provide a preview of emerging technologies, and estimate the commercial market potential for existing and new technologies which meet environmental needs. This document will show the importance of this information to help DOE EM guide technology development, to report on the progress of the program to obtain this information, and to provide recommendations for technology development obtained to date.

CMST-CP Overview. The purpose of CMST-CP is to deliver appropriate characterization, monitoring, and sensor technology to the Office of Waste Management (EM-30), the Office of Environmental Restoration (EM-40), and the Office of Facility Transition and Management (EM-60). The technology development must also be cost effective and appropriate to EM-30/40/60 needs. Furthermore, the required technologies must be delivered and implemented when needed. Accordingly, and to ensure that available DOE resources are focused on the most important needs, management of the technology development is concentrated on the following Focus Areas:

- High-Level Waste Tank Remediation (TFA)
- Mixed Waste Characterization, Treatment, and Disposal (MWFA)
- Facility Deactivation, Decommissioning, and Material Disposition (D&DFA)
- Subsurface Contamination (SCFA)

The EM mission cannot proceed intelligently, safely, or economically unless the problems it addresses and the processes it employs are adequately characterized or monitored. A common problem is that, even in cases where currently available characterization and monitoring technologies are applicable, the costs are unacceptably high. Another is that critical characterization, monitoring, and sensor technologies needed to address several of the most important EM problems are not available, are not yet accepted by regulators, or have not been proven under EM mission conditions. Some examples of needed characterization, monitoring, and sensor technologies are listed below, by Focus Area.

TFA Safe, fast, economical methods and instruments for characterization and monitoring of the gaseous, liquid, and solid contents of high-level waste tanks to address safety questions, and for assurance of safety and quality during storage, retrieval, processing, and disposal.

MWFA Safe, fast, and economical instrumentation and methods for characterization and monitoring of mixed waste in containers and mixed waste treatment processes, effluents, and final waste forms - for assurance of worker, public, process, and facility safety, and to assure the quality and public acceptance of treatment processes and final waste forms.

SCFA Instrumentation and methods for determination of the location, nature, level, and 3-dimensional extent of Dense Non-Aqueous Phase Liquids (DNAPLs) in the subsurface; automated systems for groundwater monitoring that are both economical and accepted by the regulators.

Instrumentation and methods for establishing and monitoring the integrity of subsurface barriers and for real-time monitoring of the progress and quality of in situ stabilization processes.

D&DFA Non-laboratory instrumentation and methods for in situ identification, preferably in real time, of materials and surfaces contaminated with hazardous materials such as PCBs, U, Hg, and tritium; technologies for real-time monitoring of the progress and quality of decontamination.

Since all the Focus Areas have characterization and monitoring development needs, technology that is developed for one Focus Area can often be adapted to solve problems in another. The CMST-CP identifies technology gaps, integrates technology development, and leverages resources to achieve synergy in development and to provide cost-effective solutions. The resources include those of other federal agencies, private companies, and universities as well as those within the DOE. The priorities and schedules for CMST development and implementation conform to the directions and needs specified by the Focus Areas.

The CMST-CP promotes private sector R&D involvement through Cooperative Research and Development Agreements (CRADAs), Research Opportunity Announcements (ROAs), the Small Business Innovation Research (SBIR) program, and the Technology Reinvestment Project (TRP); collaboration with other federal agencies is promoted through interagency agreements (IAGs). The CMST-CP provides necessary coordination to promote timely and cost-effective development and implementation of needed characterization, monitoring, and sensor technologies.

The Need for Field Deployable Characterization and Monitoring Technologies. Traditional methods of characterization entail the collection and transport of samples for off-site analysis at analytical laboratories. Such analysis is expensive and time consuming. Since field operation decisions must often be made on the basis of characterization information, time and cost savings can be achieved by performing analyses with field deployable instrumentation. The needs for monitoring favor on-site instrumentation even more strongly because some applications such as process control cannot be satisfied by off-site analytical laboratories. Thus, an important goal of the CMST-CP is to provide field deployable characterization and monitoring instrumentation for use by DOE personnel and contractors (customers) who are performing site characterization, waste remediation (destruction and stabilization), and environmental restoration.

The DOE customers will choose technologies for their work which they deem best available for their needs. New technology development must carefully take into account the needs of the DOE customer as well as assure that any new field deployable instrumentation developed meets those needs and is easily implemented. Facile implementation of technology usually implies that the instrumentation must be available in commercial form so that adequate product support (instruction manuals, application notes, repair, spare parts, etc.) can be obtained readily. Therefore, new technologies must be commercial or have commercial-quality support before implementation can be assured.

Recommendation Program. Given the above considerations, CMST-CP must not only examine DOE needs in as great a detail as possible, but it must also recommend technology development actions to the point of inducing the introduction of new commercial products. To aid program managers in performing these tasks, the technical field support office for CMST-CP at Ames Laboratory, has undertaken efforts to:

- survey the needs of both DOE and commercial customers for sensors and field deployable instrumentation capable of performing on-site chemical analysis for environmental applications
- identify existing commercial products which may meet the characterization and monitoring needs of the DOE EM program
- identify emerging new technologies which may meet the characterization and monitoring needs of the DOE EM program and which have potential for commercialization
- estimate the commercial potential for new instrumentation capable of meeting identified needs

This program includes:

- the commissioning of a market study to rank needs on the basis of customer interest and then to estimate commercial potential of characterization technologies
- the organization of a Workshop to assess needs and commercial markets
- the presentation of a Forum at a major scientific meeting to publicly disseminate information and obtain feedback from the technical and commercial comunity
- the development and offering of an Internet accessible Web database containing information and links concerning existing characterization and monitoring technologies

The status and results obtained from each of these efforts are discussed in this report and used to construct recommendations for CMST-CP technology development and implementation.

CHAPTER 2

MARKET INFORMATION

Importance of Market Data. Given that successful implementation of new technologies is heavily dependent on their commercialization, it is important to establish estimates of what commercial potential exists for instrumentation which can meet the CMST-CP needs of the DOE. Technology development program managers can identify needs areas where commercial development activity may be high because DOE needs overlap with commercial needs. In such cases DOE resources can be used to encourage or leverage commercial investments to bring products to market. Minimal DOE funding may be required for development of instrumentation which will be in high commercial demand. In contrast, DOE needs which do not overlap with commercial needs may not attract sufficient investment from the private sector to allow commercialization without DOE contributions. In extreme cases, commercial potential for sales of instrumentation to meet unique DOE needs may be so small that DOE would have to fund all development and implementation activity to meet that need. Thus, technology development is heavily influenced by commercial potential.

Estimates of market potential can also be used to encourage commercial development activity in the private sector. By making commercial instrumentation developers aware of both DOE and commercial needs and of estimates of their associated market potentials, investment decisions can be made with greater confidence of success. Any reduction of risk should enhance investment in commercial ventures and increase the availability of improved instrumentation capable of meeting DOE needs.

Public Market Information. A good deal of market information on the environmental industry can be obtained from public information sources. One important source of information is the Environmental Business Institute of San Diego, CA (EBI). In an article published by EBI in the Environmental Business Journal[1], it was estimated that 1995 global sales of environmental instrumentation were $2.5b, that 46% of these sales were in the US, and that 56% ($1.4b) of the instruments were laboratory instruments and the rest (44%) were non-laboratory (field) instruments. Thus:

- Total 1995 US sales of environmental instruments were $1.2b (46% of $2.5b)
- Total 1995 US sales of laboratory environmental instruments were $672M (56% of $1.2b)
- Total 1995 US sales of non-laboratory environmental instruments were $528M (44% of $1.2b)

The above estimate of the environmental instrumentation market may not include all the equipment used in characterization and monitoring of interest to the DOE's EM division and the environmental management industry as a whole. The Global Environment & Technology Foundation of Annandale, Virginia has published 1994 data from EBI on US and Global sales of environmental related equipment and services on the Internet World Wide Web[2]. Shown in Table 2-1, are data on US Environmental Industry sales broken down by market segment from

[1] Environmental Business Journal, 8(12),1-8, Dec. 1995,
[2] The Global Environment & Technology Foundation of Annandale, Virginia, http://www.gnet.org/gnet/market/mktinfo/trends/mkttrends.htm

reference 2. In Table 2-1 it can be seen that two categories of equipment contributed to $4.0b (billion) in sales in the business segment of monitoring and assessment in 1994: instruments & information systems and waste management equipment. Both of these categories contain instrumentation which addresses DOE needs and which is within the scope of the CMST-CP technology development program.

The instruments and information system category in Table 2-1 can be broken down into its two parts and can be corrected to 1995 data by assuming a 4% growth rate[1] as follows:

- Total 1995 US sales of instruments and information systems for monitoring and assessment in 1995 can be estimated as $3.0b (104% of $2.9b).
- Total 1995 US sales of instruments for monitoring and assessment in 1995 was estimated as $1.2b[1] ($528M non-laboratory) as discussed above.
- Total 1995 US sales of information systems for monitoring and assessment in 1995 then can be estimated as $1.8b ($3.0b - $1.2b in sales of environmental instrumentation)

It should be noted that while field deployable (non-laboratory) instrumentation is of greatest interest to the DOE, information systems (which may be deployed off-site) used to support such instrumentation also represent a substantial market which may be estimated to be as high as $1.8b/yr).

The second market segment listed in Table 2-1 as waste management equipment for monitoring and assessment also represents potential sales for new characterization and monitoring technologies. A more detailed breakdown of this category into on-site and off-site equipment is not available nor is a definition of how waste management equipment differs from instrumentation in general. However, it can be argued that new technologies developed to meet DOE EM needs would address a large part of this market segment.

Additional market potential can also be forecast by assuming that some portion of the environmental analytical laboratory services market will be displaced by on-site services using field deployable instruments. Since this market sector accounted for $672M in environmental instrument sales in 1995, penetration of this market would represent additional market potential of a substantial magnitude. For example 20% penetration would increase the on-site characterization and monitoring equipment market by $134M/yr.

Given the above public market information, one can predict that field deployable commercial products based on emerging and adaptable technologies for environmental characterization and monitoring will address a market for such products that ranges in size from a conservative estimate of $528M/yr (non-laboratory instrumentation only) to a more widely based estimate of as much as $1.6b/yr (non-laboratory instrumentation plus as waste management equipment for monitoring and assessment). Ancillary information systems could add an additional $1.8b/yr in sales potential. Thus substantial commercial potential to drive commercial development of improved technologies for some DOE EM needs appears to exist.

Table 2-1
US Environmental Industry Segments by Process 1994

Business Segment→	Avoidance	Monitoring & Assessment	Control	Remediation & Restoration	1994 Total
SERVICES					
Analytical Services		1.6			1.6
Wastewater Treatment Works			25.7		25.7
Solid Waste Management			31.0		31.0
Hazardous Waste Management			6.4		6.4
Remediation/Industrial Services				8.6	8.6
Consulting & Engineering	1.5	5.2	5.0	3.5	15.3
EQUIPMENT					
Water Equipment and Chemicals			13.5		13.5
Instruments & Information Systems		2.9			2.9
Air Pollution Control Equipment			11.7		11.7
Waste Management Equipment		1.1	7.8	2.2	11.2
Process & Prevention Technol.	0.8				0.8
RESOURCES					
Water Utilities			24.2		24.2
Resource Recovery	15.4				15.4
Environmental Energy Sources	2.2				2.2
TOTAL ALL SEGMENTS:	19.9	10.8	125.4	14.4	170.5
PERCENT ALL SEGMENTS	11.7%	6.3%	73.5%	8.4%	

SOURCE: Environmental Business International, Inc., San Diego, CA, units in $bil

Market as Indicated by Site Data

An valuable approach which can indicate how the environmental instrumentation market is distributed between private, state and federal customers is to examine the distribution of waste sites between these sectors. A source of information is an Environmental Protection Agency (EPA) report on the markets and technology trends for site remediation[3] . This report discusses the number and types of sites which require remediation and which in turn also require characterization and monitoring services. Table 2-2 contains a list of the types of sites identified by the EPA and the number of sites in each category which require remediation. Additional sites where a need for remediation is suspected but not confirmed exist for all categories.

Table 2-2
Sites Requiring Remediation[13]

Site Category	Number of Sites Requiring Remediation
National Priority List (NPL) (Superfund) Sites (9/30/92)	1,235
RCRA Regulated Hazardous Waste sites	1,500 to 3,500
Underground Storage Tank (UST) Sites	360,000
DOD Sites	7,313
DOE Sites	~4000
Civilian Federal Agency Sites	925
State Hazardous Waste Sites	69,808
Private Party Sites	large but unknown, 1991 remediation market estimated as $1 billion, implying >140,000 sites based on state hazardous waste site expenditures
TOTAL	>585,000

The data of Table 2-2 indicate that the responsible parties for a large majority of sites requiring remediation are non-DOE and non-federal. This fact in turn implies that the market will be dominated by non-federal needs and customers. Indeed, DOE requirements may represent less than 1% of the entire market, as indicated by number of sites requiring remediation.

Focused Market Study. The existence of a substantial market is encouraging for the prospect of developing new on-site field deployable technologies. However, little detailed information exists to connect specific needs and particular technologies with significant shares of this market. Unfortunately, analysis of the market at this level of detail is a very large task which would require substantial resources. However, by examining a smaller, limited sector of the entire environmental instrumentation market, one can obtain more detail about the distribution of commercial potential over needs and technologies which can be extrapolated (with some loss of reliability) to the entire market. This strategy was employed by commissioning a market study focused only on the waste and site characterization segment of the market.

The Ames laboratory CMST-CP technical field support office issued a Request for Proposal (RFP) to solicit a market study to determine:

- what needs and field applications are most common

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[3] “Cleaning Up the Nation’s Waste Sites: Markets and Technology Trends”, Environmental Protection Agency, EPA/542/R-92/012, April 1993.

- what commercial instrumentation is currently being used for environmental characterization analysis in the field
- what new capabilities for chemical analysis in the field would be most valuable to users working in the area of environmental management
- what is the market for commercial environmental characterization instrumentation
- what is the market potential for new technologies

The responder chosen to conduct the market study was the Unimar Group of Alton, IL. Unimar was given prioritized lists of DOE needs prepared by the DOE EM-50 Focus Areas as well as a previous set of reports on commercially available environmental instrumentation prepared for CMST[4]. EM-50 technology summary booklets were also provided.

Primary data was obtained by conducting interviews with developers and users of environmental instrumentation. Over thirty non-DOE equipment users were contacted in regard to the field instrumentation which they use, the manner in which it is employed, and the characteristics most desirable in new instrumentation. Twenty interviews were conducted regarding the use of field instrumentation for site and waste characterization. Fourteen individuals were contacted regarding the use of field instrumentation for the monitoring of environmental remediation processes. Additional secondary research material was collected from industry publications, books, periodicals, buyer's guides, and the Internet.

The resulting market study by Unimar was presented in preliminary form at the Workshop and Forum held as part of this program, and the final form has been published on the Internet Web[5]. This market study is also included as Appendix A along with a critique of the market study written by its authors after the study's completion. The conclusion of the market study was that the sector of the market studied in detail, waste and site characterization, currently generates $140M/yr of instrumentation sales with short term growth rate forecast at 7%. This sector obviously is only a small segment (~5%) of the entire environmental equipment market.

Unimar also compiled a list of ranked needs for site and waste characterization and estimated the percent of the market segment each needs represented. A list of the higher ranked needs and estimated potential market share is presented in Table 2-2. Methods used to estimate and apportion market potential to needs are discussed in the Unimar report[4].

Additional consideration of needs was pursued at the Workshop. In Ch. 3, the entire list of needs compiled by Unimar is compared with an independent needs assessment done by the Workshop participants and trends in the data are discussed.

[4] "Literature Search, Review, and Compilation of Data for Chemical and Radiochemical Sensors", Hazwrap Reports DOE/HWP- 130,133,138,144,149,152,153.

[5] htttp://cmst.ameslab.gov/CMST/Market_Study.html

Table 2-2
Needs Ranked by Percent of Market Potential

13%	Detecting individual organics in air	0.6%	Monitoring other contaminants in air
12%	Detecting individual organics in soil	0.6%	Detecting DNAPLs in soil
7.0%	Detecting individual organics in water/ liquids	0.6%	Monitoring individual RCRA metals in water
6.1%	Detecting individual RCRA metals in soil	0.5%	Detecting DNAPLs in water
5.7%	Detecting individual organics in soil in-situ	0.4%	Detecting individual radioactive metals in air
4.9%	Detecting individual RCRA metals in water	0.4%	Detecting individual radioactive metals in sludge
4.8%	Detecting individual RCRA metals in water in-situ	0.4%	Monitoring other contaminants in soil
4.8%	Detecting individual RCRA metals in soil in-situ	0.4%	Monitoring other contaminants in water
4.0%	Detecting individual organics in water in-situ	0.4%	Monitoring individual organics in soil in-situ
3.2%	Detecting individual RCRA metals in air	0.2%	Monitoring other contaminants in sludge
3.2%	Detecting individual RCRA metals in sludge	0.2%	Detecting individual RCRA metals in asbestos
2.8%	Detecting other contaminants in soil in-situ	0.2%	Detecting individual RCRA metals in facilities remotely
2.7%	Detecting other contaminants in water in-situ	0.2%	Detecting individual RCRA metals in metal, concrete, other solids
2.6%	Detecting other contaminants in soil	0.2%	Detecting RCRA metals in waste drums & boxes non destructively
2.6%	Detecting individual organics in air in-situ	0.2%	Monitoring individual RCRA metals in soil in-situ
2.6%	Detecting individual organics in sludge	0.2%	Detecting individual organics in asbestos
2.3%	Detecting other contaminants in water	0.2%	Detecting individual organics in facilities remotely
1.7%	Monitoring individual organics in air	0.2%	Detecting individual organics in metals, concrete, other solids
1.4%	Monitoring individual organics in soil	0.2%	Detecting organics in waste drums and boxes non destructively
1.0%	Detecting individual radioactive metals in soil	0.2%	Detecting total organic carbon content in tank waste
0.9%	Detecting individual radioactive metals in water	0.1%	Monitoring other contaminants in soil in-situ
0.9%	Monitoring individual RCRA metals in air	0.1%	Monitoring individual radioactive metals in air
0.8%	Monitoring individual organics in water	0.1%	Monitoring individual radioactive metals in soil
0.8%	Monitoring individual RCRA metals in soil	0.1%	Monitoring individual organics in water in-situ
0.6%	Detecting DNAPLs in soil in-situ	0.1%	Monitoring individual radioactive metals in water
0.6%	Detecting individual radioactive metals in soil in-situ		
0.6%	Detecting DNAPLs in water in-situ		
0.6%	Detecting individual radioactive metals in water in-situ		
0.6%	Detecting individual radioactives in high level waste tanks in-situ		

13% Detecting individual organics in air	0.6% Monitoring other contaminants in air
12% Detecting individual organics in soil	0.6% Detecting DNAPLs in soil
7.0% Detecting individual organics in water/ liquids	0.6% Monitoring individual RCRA metals in water
6.1% Detecting individual RCRA metals in soil	0.5% Detecting DNAPLs in water
5.7% Detecting individual organics in soil in-situ	0.4% Detecting individual radioactive metals in air
4.9% Detecting individual RCRA metals in water	0.4% Detecting individual radioactive metals in sludge
4.8% Detecting individual RCRA metals in water in-situ	0.4% Monitoring other contaminants in soil
4.8% Detecting individual RCRA metals in soil in-situ	0.4% Monitoring other contaminants in water
4.0% Detecting individual organics in water in-situ	0.4% Monitoring individual organics in soil in-situ
3.2% Detecting individual RCRA metals in air	0.2% Monitoring other contaminants in sludge
3.2% Detecting individual RCRA metals in sludge	0.2% Detecting individual RCRA metals in asbestos
2.8% Detecting other contaminants in soil in-situ	0.2% Detecting individual RCRA metals in facilities remotely
2.7% Detecting other contaminants in water in-situ	0.2% Detecting individual RCRA metals in metal, concrete, other solids
2.6% Detecting other contaminants in soil	0.2% Detecting RCRA metals in waste drums & boxes non destructively
2.6% Detecting individual organics in air in-situ	0.2% Monitoring individual RCRA metals in soil in-situ
2.6% Detecting individual organics in sludge	0.2% Detecting individual organics in asbestos
2.3% Detecting other contaminants in water	0.2% Detecting individual organics in facilities remotely
1.7% Monitoring individual organics in air	0.2% Detecting individual organics in metals, concrete, other solids
1.4% Monitoring individual organics in soil	0.2% Detecting organics in waste drums and boxes non destructively
1.0% Detecting individual radioactive metals in soil	0.2% Detecting total organic carbon content in tank waste
0.9% Detecting individual radioactive metals in water	0.1% Monitoring other contaminants in soil in-situ
0.9% Monitoring individual RCRA metals in air	0.1% Monitoring individual radioactive metals in air
0.8% Monitoring individual organics in water	0.1% Monitoring individual radioactive metals in soil
0.8% Monitoring individual RCRA metals in soil	0.1% Monitoring individual organics in water in-situ
0.6% Detecting DNAPLs in soil in-situ	0.1% Monitoring individual radioactive metals in water
0.6% Detecting individual radioactive metals in soil in-situ	
0.6% Detecting DNAPLs in water in-situ	
0.6% Detecting individual radioactive metals in water in-situ	
0.6% Detecting individual radioactives in high level waste tanks in-situ	

Market Conclusions. Public information can be used to estimate the sales of field deployable instrumentation for environmentally related characterization and process monitoring tasks in all sectors of the US economy as $2.8b/yr for 1995. However, detailed information as to which particular characterization and monitoring needs generate the largest shares to this market and as to what technologies have the potential to most effectively compete for sales in this market does not appear to be readily available.

To obtain a more detailed analysis of the market, a market study was used to examine a small segment of the market of particular interest to the DOE, site and waste characterization. Results of the market study indicate that site and waster characterization only account for $140M/yr in instrument sales. Thus, the bulk of the market lies in the process monitoring market where more detailed market analyses do not appear to be publicly available.

The market study did provide primary interview data and secondary research into the environmental instrumentation technologies currently in use and more detailed analysis of environmental characterization needs as well as market estimates. The needs and technology information documented by the market study was further developed at the Workshop. Results of market study and Workshop discussions of needs and technologies are described in subsequent chapters of this report and are ultimately used to recommend technology development strategy.

CHAPTER 3

NEEDS FOR CHEMICAL SENSORS AND FIELD DEPLOYABLE INSTRUMENTATION FOR ENVIRONMENTAL APPLICATIONS

Needs Definitions. A great variety of needs arise from the requirements of characterizing environmentally contaminated sites and of monitoring the processes of remediation, restoration and pollution prevention. Many different contaminants must be detected and/or quantified, and the types of contaminants commonly encountered varies between sites and between the government and private sectors. Contaminants may be found in a variety of sample matrices (e.g. air, water, soil), and the concentrations of interest may vary over a wide range of magnitudes from the percent level to parts per billion (ppb) or lower. Assay requirements also vary greatly. Analyses of contaminants designed to meet regulatory requirements must be done with good accuracy and precision. Screening and control applications may require less stringent accuracy and precision but may demand more rapid and more frequent (or even continuous) assays. Some applications require analyses of hazardous materials or components in a hazardous sample matrix or hazardous environment where remote sampling and instrument operation is most desirable.

Effective design of new technologies to meet the needs of environmental characterization and monitoring requires the definition of these needs to as great extent as possible. The process of obtaining these definitions appears to be slow and difficult. The Focus Areas of EM-50 continue to assess and refine the needs of the DOE. Definition of the needs of the commercial sector is less complete. To address this problem, two approaches were taken to create a list of needs relevant to both the DOE and the commercial sectors. As part of the market study, Unimar Group cataloged DOE needs from Focus Area listings and surveyed commercial field operators and instrument manufacturers. Secondly a Workshop on the commercialization of Chemical Sensors and Field Deployable Instrumentation was held to independently assess needs from a group of scientists and engineers representing technology developers, technology commercializers, and end users as described in the next section. The results of these assessments are discussed in latter sections this chapter. In addition, updated needs statements have recently been issued by the Focus Areas, and these are discussed relative to market potential in the final section of this chapter.

Workshop Organization.

The Workshop on Chemical Sensors for Environmental Applications was held March 1 and 2, 1996, immediately prior to the Pittsburgh Conference (PittCon) in Chicago. Pittcon is a major international scientific meeting covering the areas of analytical chemistry and applied spectroscopy and consists of a large number of technical presentations in conjunction with a very large exhibit of scientific analytical instrumentation. The Workshop was timed to attract individuals participating in PittCon and was intended to serve as a major source of new information and ideas for all parties interested in the development, commercialization, and use of analytical, field deployable technologies for environmental applications.

Users, developers, and manufacturers of chemical sensors and field deployable analytical instrumentation were invited to participate in this Workshop to discuss all the issues of developing, adapting, and commercializing analytical instrumentation technologies for environmental analysis. The objectives of both the Workshop and Forum were to:

- identify developing and existing sensor technologies appropriate for EM field deployable environmental analysis and sensing
- determine the present and potential market demand for commercial field deployable environmental analysis instrumentation
- publicize market information relevant to commercial field deployable environmental analysis instrumentation
- prioritize and promote the commercialization of technologies to meet the needs of EM and private sector applications

Individuals were invited to the Workshop with the goal of obtaining a group of people which could give good perspective and feedback on recommendations for the development and commercialization of chemical sensors and field deployable instrumentation. Participants whose knowledge and expertise fell into the following four categories were invited:

- **Technologists**. Individuals with technical expertise working in the research laboratory environment to develop or improve technologies for chemical sensors and field deployable instrumentation. 25 attendees fell within this category with at least two people representing each of following five classes of sensors and instrumentation:
    - ♦ Optical sensors
    - ♦ Electrochemical Sensors
    - ♦ Piezoelectric Mass Sensors
    - ♦ Immunosensors
    - ♦ Field Usable Instrumentation and Methodology
- **Environmental Service Providers and Site Personnel**. "Hands-on" individuals who supervise or do environmental characterization work in the field as well as individuals who make buying decisions with regard to instrumentation for environmental characterization and monitoring. While many people in this category were invited from the DOE and from contractors, the acceptance rate was low, and 8 individuals in the class were present. This group was somewhat under-represented.
- **Vendors**. Marketing managers with a technical background from commercial instrumentation providers are desired. A large response was received from this group. 36 people from this classification attended.
- **Technology Development Staff**. Individuals who are involved in selecting and promoting new technologies DOE environmental characterization and monitoring needs. 15 people associated with DOE Focus Areas, CMST-CP, and the market study subcontractor

A total of 84 people attended the Workshop which lasted for 1.5 days.

Workshop Needs Evaluation. The first half day of the Workshop, information was given to the attendees regarding the CMST-CP program and preliminary market study results, including an unranked set of 68 needs identified from DOE and non-government sources. These needs are listed in Table 3-1.

Table 3-1
Unranked Needs Collected in Market Study

Need for an improved sensor for detecting (47 needs)
Detecting individual radioactive metals in air
Detecting individual radioactive metals in water
Detecting individual radioactive metals in water in-situ
Detecting individual radioactive metals in soil
Detecting individual radioactive metals in soil in-situ
Detecting individual radioactive metals in sludge
Detecting individual radioactive metals in metal, concrete, other solids
Detecting individual radioactive contaminants in facilities remotely
Detecting radioactive metals in waste drums and boxes non destructively
Detecting individual radioactive metals on underwater concrete surfaces
Detecting individual radioactive metals in asbestos
Detecting minor radioactive constituents in solution with high transuranics
Detecting individual radioactives in high level waste tanks in-situ
Detecting physical properties of high level waste in tanks
Detecting radiological properties 3D mapped in field
Detecting individual RCRA metals in air
Detecting individual RCRA metals in water
Detecting individual RCRA metals in water in-situ
Detecting individual RCRA metals in soil
Detecting individual RCRA metals in soil in-situ
Detecting individual RCRA metals in sludge
Detecting individual RCRA metals in metal, concrete, other solids
Detecting RCRA metals in waste drums and boxes non destructively
Detecting individual RCRA metals in asbestos
Detecting individual RCRA metals in facilities remotely
Detecting chemical properties 3D mapped in field
Detecting individual organics in air
Detecting individual organics in air in-situ
Detecting individual organics in water/ liquids
Detecting individual organics in water in-situ
Detecting individual organics in soil
Detecting individual organics in soil in-situ
Detecting individual organics in sludge
Detecting individual organics in metals, concrete, other solids

Table 3-1
Unranked Needs Collected in Market Study - Continued

Detecting organics in waste drums and boxes non destructively
Detecting individual organics in asbestos
Detecting individual organics in facilities remotely
Detecting total organic carbon content in tank waste
Detecting DNAPLs in soil
Detecting DNAPLs in soil in-situ
Detecting DNAPLs in water
Detecting DNAPLs in water in-situ
Detecting other contaminants in water
Detecting other contaminants in water in-situ
Detecting other contaminants in soil
Detecting other contaminants in soil in-situ
Detecting general contaminants in drums and boxes in-situ
Need for an improved sensor for monitoring (21 needs)
Monitoring individual radioactive metals in air
Monitoring individual radioactive metals in water
Monitoring individual radioactive metals in water in-situ
Monitoring individual radioactive metals in soil
Monitoring individual radioactive metals in soil in-situ
Monitoring individual RCRA metals in air
Monitoring individual RCRA metals in water
Monitoring individual RCRA metals in water in-situ
Monitoring individual RCRA metals in soil
Monitoring individual RCRA metals in soil in-situ
Monitoring individual organics in air
Monitoring individual organics in water
Monitoring individual organics in water in-situ
Monitoring individual organics in soil
Monitoring individual organics in soil in-situ
Monitoring DNAPLs in water in-situ
Monitoring other contaminants in air
Monitoring other contaminants in water
Monitoring other contaminants in soil
Monitoring other contaminants in soil in-situ
Monitoring other contaminants in sludge

The attendees were then broken into discussion groups classified by different types of needs as follows:

1. Subsurface Characterization
2. Containment Monitoring
3. Surface Decontamination for D&D Applications
4. Air Quality Monitoring
5. Effluents Monitoring
6. Process Monitors & Control / Resource Recovery
7. Wastes Characterization

Each discussion group was asked to rank significant needs in their area using the market study list, grouped by classification, as a starting reference and for each significant need, identify: baseline technologies in use, desired technology performance characteristics and commercial potential for technologies meeting that need. On the morning of the second day, discussion leaders from each group presented their findings to the workshop group as a whole. Each group presented a ranked needs list and provided for many needs information with regard to baseline technologies, emerging technologies and performance expectations. Appendix B contains the lists and comments made by each workgroup.

The relatively short time available for general discussion limited validation and discussion of the information provided for the individual needs by the entire group. Also, well justified estimates of the commercial potential for the sale of instruments capable of meeting individual needs were not obtained in most cases. Many times the participants did not have the knowledge to provide estimates. In other cases, participants with good marketing information did not share their knowledge because it was considered proprietary.

One useful product of the general discussion was a condensation of ranked needs prepared by combining the ranked needs lists of each workgroup. Consensus was reached in the general discussion that this condensed list of ranked needs reasonably reflected the requirements of current environmental characterization and monitoring activities. This list is contained in Table 3-2.

A comparison of the ranked needs list from the market study in Table 2-2 and the needs list generated independently by the Workshop in Table 3-2 shows a good deal of similarity between the two lists. The analysis of organic compounds in air, water and soil is a high priority in both cases. The next highest priority is the characterization and monitoring of inorganic compounds and RCRA metals in the environment. (RCRA metals are the toxic and heavy metals identified in the Resource Conservation and Recovery Act for regulation). The general trend of market potential as a function of needs is illustrated in Figure 3-1. The relative importance of different sample matrices (air, water soil) to market potential could not be assigned. However it is clear that field instrumentation that can characterize or monitor organic compounds have the highest commercial potential for sales to service environmental applications.

Table 3-2
Ranked Needs Prepared by Workshop

Group	Need
1a, 2a	Detecting individual organics in soil in-situ
1b, 2b	Detecting individual organics in water in-situ
7	Detecting individual organics (inorganics) in air- in-situ (i.e., tank headspace)
6a	Monitoring organics/RCRA metals in water
5a	Detecting (analyzing) individual organics in water/ liquids
1c, 2c	Detecting individual organics in soil
4a	Point source characterization of 189 HAPS and point source near-real-time monitoring of a subset of HAPS (Air Quality Monitoring)
4b	Remote sensing (Air Quality Monitoring)
4c	Indoor/workplace characterization & monitoring aerial measurements (Air Quality Monitoring)
3c	Detecting individual RCRA metals in metal, concrete, other solids
5b	Detecting (analyzing) individual RCRA metals in water
5c	Detecting (analyzing) inorganics and other contaminants in water
6c	Monitoring radioactive materials in mixed, condensed phase (DOE specific)
3a	Detecting individual radioactive metals in metal, concrete, solids
3b	Detecting individual radioactive metals in asbestos
7	Detecting individual radioactive metals in sludge
7	Detecting radioactive metals in waste drums and boxes non-destructively
7	Detecting individual radioactives in high-level waste tanks in-situ
7	Detecting RCRA metals in waste drums and boxes non-destructively

1. Subsurface Characterization; 2. Containment Monitoring; 3. Surface Decontamination for D&D Applications; 4. Air Quality Monitoring ; 5. Effluents Monitoring; 6. Process Monitors & Control / Resource Recovery; 7. Wastes Characterization

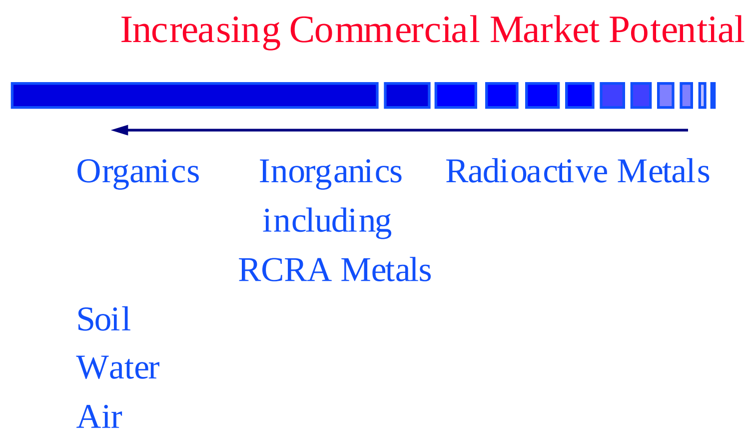

Figure 3-1

Conclusions. A significant number of needs for environmental characterization and monitoring have been identified from a user survey and from DOE documentation. These needs overlap one another in many cases. Many needs are not well documented in terms of why existing technologies are insufficient to meet requirements and in terms of what the technical performance requirements are. The commercial potential for the sale of instruments to both the government and private sectors to meet these needs is also not well established.

Relative rankings with respect to commercial potential represented by various needs in the limited area of waste and site characterization were estimated from survey results and secondary research by the Unimar Group. Independently a similar set of needs rankings was constructed from discussions at the Workshop for the broader area of environmental characterization and monitoring. These rankings, however, only indicate trends and can not be used alone to justify investment in the development of a particular technology aimed to meet specific needs. The ranked needs however do provide a strong indication of the types of needs that will be most likely to attract commercial development of new technologies.

Improved definitions of the significant needs are still required. The compilations of workgroup comments in Appendix B provide some information about current baseline methods and performance specifications. However, more complete information will most likely be required before significant commercial investment can be expected. The workgroup discussions represent a first step in the direction of greater definition and may serve as a foundation for more detailed investigations in the future.

Assessment of Needs Overlap

The focus of DOE's EM technology development efforts must, of course, be on the high priority needs of the DOE EM effort. The identification and prioritization of the EM needs for new technology development is done primarily by the EM-50 Focus Areas and Crosscutting Programs. CMST-CP works closely with all the Focus Areas to discuss needs involving characterization, monitoring and sensor technology in as great a detail as possible. A very relevant and current description of the high priority needs in the CMST area appeared in the May

1996 Research Opportunity Announcement[6] (ROA) issued by Morgantown Energy Tech. Center (METC). The ROA is a solicitation to industry for applied research designed to meet high priority EM needs. The needs described for the CMST-CP area are reproduced in Table 3-3.

To estimate the overall commercial potential of these needs, each need is assigned to one or more of the need categories contained in Table 2-2 which lists needs ranked by market potential. These needs categories and their estimated percentage of the total market potential for site and waste characterization are included in the second column of Table 3-3.

From this comparison it can be seen that several DOE needs overlap with commercial needs with significant market share, e.g. an improved VOC monitor. Other needs are so specialized that their market potential is small and principally generated by the existence of the DOE need itself. Based on this comparison, strategies for technology development can be recommended depending upon expected levels of non-DOE demand for product.

[6] ROA and information package available on the Internet at http://www.metc.doe.gov/business/solicita.html

Table 3-3A

A. High-Level Waste Tank	% Market Potential	Need Categories
Technologies are needed to provide the sampling systems, in-situ sensors, and deployment equipment required to provide the necessary physical, chemical, and radiochemical characterization information for tank waste, plus tank waste samples to support process control; safety issue resolution; and treatment, storage, and disposal decisions.	2.6% 0.6%	Detecting other contaminants in soil Detecting individual radioactives in high level waste tanks in-situ
Development of remote analytical scanning equipment is also needed to reduce the cost and time to characterize extruded cores from tank wastes. Assembly-line, remote core-scanning techniques are needed to increase laboratory capacity dedicated to tank waste analysis.	0.6%	Detecting individual radioactive metals in soil in-situ
The in-situ characterization of tank waste can be more accurate than hot cell analysis, because it eliminates time delay between sample removal and sample analysis. Intrusive sampling systems are needed which are capable of withstanding a variety of environments from strong alkaline (pH 13.5) to strong acidic (pH of 2.5); radiation levels up to 5,000 rad/hr; and temperature up to 200 °C.	0.6%	Detecting individual radioactives in high level waste tanks in-situ
In-situ measurements are needed to determine moisture, radiation levels and spectra, rheological properties, chemical speciation, physical properties, gas generations rates and types, and real-time, head-space gas build-up (hydrogen, ammonia, and nitrous oxide).	4.8% 0.6% 1.7% 0.6%	Detecting individual RCRA metals in soil in-situ Detecting individual radioactives in high level waste tanks in-situ Monitoring individual organics in air Monitoring other contaminants in air
In situ techniques that can be deployed by a cone penetrometer, a core drilling truck, or other devices that provide adequate penetration thrust through saltcake, are sought for imaging the spatial variability of tank waste content to determine chemical and radiological characteristics.	6.1% 2.8%	6.1% Detecting individual RCRA metals in soil 2.6% Detecting other contaminants in soil in-situ
Development of sensors to obtain stratigraphic layering information during core sampling operations to improve the sampling recovery rate.		

Table 3-3B

B. Subsurfance Contamination		
There is a need for the development of sensors for use with CPT tools for real-time determination of metal and radioactive contaminants in soils and groundwater.	4.8% 0.6%	Detecting individual RCRA metals in soil in-situ Detecting individual radioactive metals in soil in-situ
Innovative methods for locating and determining the distribution of residual dense non-aqueous phase liquids (DNAPLs) in the subsurface are needed.	5.7% 4.0% 0.6% 0.6%	Detecting individual organics in soil in-situ Detecting individual organics in water in-situ Detecting DNAPLs in soil Detecting DNAPLs in water in-situ
Soil washing requires real-time input to identify waste from nonwaste, to segregate wastes for designated processes, and to determine the efficiency of cleanup operations. There is a need for the development of sensors for monitoring of hazardous metals and radioactive contaminants (U and Pu) in real-time during the soil washing process.	4.8% 0.2%	Detecting individual RCRA metals in soil in-situ Monitoring individual RCRA metals in soil in-situ
Techniques and methods are sought to evaluate emplaced subsurface barriers to detect the location and measure the magnitude of barrier discontinuities that may exist on a micro-scale (fractions of an inch).		
Barrier monitoring techniques are needed that enable observations or predictions of loss of barrier performance. Parameters measured must be related to barrier performance, must be defined and must describe how they will be analyzed and quantified, and explain how they relate to barrier performance.	0.4%	Monitoring other contaminants in soil
Data integration systems that meld multiple physical and chemical parameters to provide information on waste sites before and during remedial action are needed		
Sensors are needed for use with digface characterization tools to prevent accidental rupture and spread of buried, containerized wastes, and to determine when to stop excavating.	5.7% 4.8% 2.8%	Detecting individual organics in soil in-situ Detecting individual RCRA metals in soil in-situ Detecting other contaminants in soil in-situ

Table 3-3C

C. Decontamination and Decommissioning		
Techniques that provide the capability to image a large area to determine plutonium residues in soils and on concrete and metal surfaces.	0.6% 0.2%	Detecting individual radioactive metals in soil in-situ Detecting individual RCRA metals in facilities remotely
Nondestructive techniques for measurement of trace quantities of Tc, U, and RCRA-listed metals on the internal surfaces of carbon steel or stainless steel pipes with diameters ranging from 1-17" inches and wall thicknesses from 0.25-0.5".	0.2%	Detecting individual RCRA metals in facilities remotely
Characterization methods are needed to determine the extent of contamination, (from RCRA metals and radionuclides) and for tracking progress in decontamination operations. These field analysis methods are needed for assessing the depth profile of contamination in concrete and other porous surfaces, as well as contamination levels in cracks, crevices, and joints in other structural materials. Analysis methods are needed that are minimally intrusive and generate little or no secondary waste.	0.2% 0.2%	Detecting individual RCRA metals in metal, concrete, other solids Detecting individual RCRA metals in facilities remotely
Radon, an alpha particle emitter, is emitted from the native soils or building materials and interferes with alpha radiation readings for other alpha particle emitters (e.g., uranium, thorium). There is a need for a real-time, alpha-radiation air monitor that discriminates between radon emissions and other alpha emitters.	0.4%	Detecting individual radioactive metals in air
There is a need for on-line, real-time sensors that could be attached to commercial or near-commercial decontamination technologies to provide continuous or nearly continuous feedback on the effectiveness of decontamination	0.2% 0.2% 0.1% 0.1%	Monitoring individual RCRA metals in soil in-situ Detecting individual RCRA metals in metal, concrete, other solids Monitoring individual radioactive metals in air Monitoring individual radioactive metals in soil

Table 3-3C Continued

There is a need for real-time sensors to sort waste as it is generated according to its hazard level (i.e., TRU, LLW, HLW, RCRA, Mixed, Not contaminated).	0.2% Monitoring individual RCRA metals in soil in-situ 0.1% Monitoring individual radioactive metals in soil
There is a need for monitors or sensors to assess the structural integrity of the buildings and their contents. These monitors or sensors will provide information on which facilities require immediate removal or maintenance to keep the facilities from structural failure.	

Table 3-3D

D. Mixed Waste Characterization, Treatment, and Disposal	
There is a need for the development of sensors for monitoring of hazardous metals and radioactive contaminants (U and Pu) in real-time during environmental restoration activities.	0.9% Monitoring individual RCRA metals in air 0.2% Monitoring individual RCRA metals in soil in-situ 0.6% Monitoring individual RCRA metals in water 0.1% Monitoring individual radioactive metals in air 0.1% Monitoring individual radioactive metals in soil
Continuous emission monitoring in offgas systems for thermal and non-thermal processes will be critical in ensuring the success of treatment technologies. The EPA is proposing new rules for thermal treatment processes that will demand expanded capability for monitoring offgases. These expanded monitoring capabilities should facilitate permitting and public acceptance of these treatment processes. For VOCs, heavy metals, alpha particles, and mercury, the identified deficiency relates to the current lack of continuous emission monitors and the fact that real-time monitoring is not possible.	

Table 3-3D Continued

An improved VOC monitor incorporating one or more of the following features: a) continuous, real-time analysis of VOCs in an offgas containing organics, metals, particulate, and radionuclides; (b) speciation between different organics; and (c) have a sensitivity of at least 1 ppb. The instrument would be more cost-effective, compact, require little maintenance, and generate no waste.	13% 1.7%	Detecting individual organics in air Monitoring individual organics in air
An improved off gas monitor for heavy metals would incorporate one or more of the following features: (a) continuous, real-time analysis of multiple metals; (b) speciation between different metals; and (c) sensitivity at least 5 μg/m3 except for beryllium (0.5 μg/m3), lead (50 μg/m3), and selenium (50 μg/m3). The instrument would be more cost-effective, compact, require little maintenance, and generate no waste.	3.2% 0.9%	Detecting individual RCRA metals in air Monitoring individual RCRA metals in air
An improved monitor for alpha contamination would incorporate the following features: (a) continuous, real-time analysis of alpha contamination in an offgas containing organics, metals, particulate, and radionuclides; and (b) sensitivity less than 1 pCi/l with an integration time of less than one minute. The instrument would be cost-effective, compact, require little maintenance, and generate no waste.	0.4% 0.1%	Detecting individual radioactive metals in air Monitoring individual radioactive metals in air
Data integration systems that meld multiple physical and chemical analytical parameters to provide information on waste forms and contaminants for waste certification and for characterization prior to treatment.		
Radioactive waste assay systems for field application for below grade containerized or loose waste (find "hot spots")	0.6%	Detecting individual radioactive metals in soil in-situ

Table 3-3D Continued

An improved system for mercury monitoring in an off gas would incorporate one or more of the following features: (a) continuous, real-time analysis of an offgas containing VOCs, metals, particulate, and radionuclides; (b) speciation between elemental mercury and reacted forms; and (c) sensitivity of at least <5 μg/m3. It would operate continuously, providing real-time data for control. The instrument would be more cost-effective, compact, require little maintenance, and generate no waste.	3.2% 0.9%	Detecting individual RCRA metals in air Monitoring individual RCRA metals in air
Minimally intrusive, cost effective chemical and radionuclide analysis techniques for application in surface waste disposal units.	1.0%	Detecting individual radioactive metals in soil
Improved NDE methods are required that are nonintrusive, nondestructive, operate at-line or on-line, generate data real-time (i.e. <15 minutes), and are readily employed in a glove-box environment. There is also a need for the capability for NDE of large containers, such as 4ft x 4ft x 8ft boxes. Systems are needed that provide elemental analysis (such as C, H, Cl, N, etc.), BTU content, as well as RCRA metal content. The methods must be compatible with the waste material types (e.g. debris, sludges, liquids) and meet all QAPP and EPA SW-846 requirements	4.8% 4.8% 2.8% 2.7% 0.2% 0.2%	Detecting individual RCRA metals in water in-situ Detecting individual RCRA metals in soil in-situ Detecting other contaminants in soil in-situ Detecting other contaminants in water in-situ Detecting individual RCRA metals in metal, concrete, other solids Detecting RCRA metals in waste drums & boxes non destructively
Improved non-destructive assay (NDA) systems are needed that provide increased sensitivity, more effectively deal with fissile material composition, isotopic distribution, and waste matrix material types. Improved systems must be able to demonstrate compliance with all QAPP requirements for specific waste types.	1.0% 0.4%	Detecting individual radioactive metals in soil Detecting individual radioactive metals in sludge
Improved container integrity remote sensors or techniques are needed to nondestructively determine drum wall thickness, and to verify compliance with DOT Type A requirements. Techniques must be operable on corroded drums without cleaning and determine wall thickness around the circumference at a minimum of eight vertical locations. Examination must be demonstrated to be practically useful on thousands of drums per year.		

CHAPTER 4

TECHNOLOGIES TO MEET THE NEEDS FOR ENVIRONMENTAL CHARACTERIZATION AND MONITORING

Strategies to Identify Baseline and Emerging Technologies.

Many technologies already exist to meet the needs for environmental characterization and monitoring. However, many of these methods may be inefficient, slow, or expensive, and/or may require use of instrumentation off-site. To properly decide what new technologies should be developed, an understanding of the status and shortcomings of technologies in use must be obtained. In addition, an incomplete knowledge of what technologies are commercially available may prevent field users from implementing the best, fastest, and/or cheapest methods possible. Finally, adaptations of existing technologies may prove, in some cases, to be an efficient approach to obtaining effective field deployable methods. For all these reasons, it is important to establish what existing baseline technologies are available and are in use.

Assuming needs can be identified where baseline technologies are not available or are not satisfactory, then a thorough knowledge of new and emerging technologies and their potential applications is required to properly identify methods which can better meet the identified needs. Emerging technologies ranging from laboratory prototypes to new commercial products should be of interest.

In this program, several approaches are being used to identify baseline and emerging technologies. These strategies include: a compilation of database information on existing commercial technologies, inclusion of data on field instrument use in the market study, and discussion of emerging technologies as a major activity of the Workshop. These approaches are described below.

Compilation of Database Information. To assist DOE customers in the selection of the best available technologies to meet their specific needs, the CMST-CP is developing an Internet Guide to aid in the selection of field-worthy chemical sensors and instrumentation for environmental measurement applications. These applications can be in support of site characterization activities, monitoring remediation and removal actions, waste processing monitoring, final waste forms characterization, remote long term sensing applications, or any environmentally-related measurement activities that support useful decision-making.

The purpose of this non-traditional database is to provide resource information pointers that will facilitate users in making informed decisions on the most suitable instrumentation to solve their environmental CMST measurements needs. The database design features are that it is: 1) dynamic, 2) methods and applications driven, 3) composed of sources and references to existing databases, 4) focused only on complete instrumental measurement systems. Vendors can update their information pointers at any time via direct World Wide Web access. The vendor's information applications pages are directly linked to user's measurement needs through the problem definition database search. Additionally, technologies used to perform analysis of particular analytes in particular sample matrices at specified levels are identified through analytical methods (e.g., EPA SW846 Methods or DOE Methods for Evaluating Environmental and Waste Management Samples). Existing databases that identify technologies for environmental applications are referenced and when available hotlinked. Such databases include EM BEST, TechCon, GJPO

Commercial Environmental Cleanup Directory, GNET, EPA Vendor FACTS, SITE and Dual-Use programs.

The primary goal of the effort is to provide a fast and effective search for suitable technologies to solve DOE's environmental measurement needs. The user's search of a defined measurement problem provides a manageable subset of vendors to contact using on-line WWW access that is available 24 hours a day. The Vendor Information input WWW pages are ready for inputting data and search capabilities are being developed. A CMST vendor's database start page is being developed to allow users to browse instrumentation by vendor product category, or browse selected standard methods by analyte and sample. A CMST Forum has been set up on the GNET WWW pages. Additionally, a collaborative effort with the Ames Laboratory Applied Mathematics Program will be made to develop smart search routines for select electronic databases and a selected set of WWW "bookmarks" to automatically add and update new information. The targeted users of this database are:

- anyone with an environmental measurement need who wants to find out WHAT ARE THE AVAILABLE TECHNOLOGIES for the application;
- anyone who must Recommend, Specify, or Approve instrumentation purchases;
- anyone who wants to check the list of vendors that make a certain product;
- anyone who wants to see which vendor emphasize environmental applications;
- anyone who wants to consider alternatives to their current technology.

Vendor-supplied information and source-referenced input from existing databases allow users to quickly find a manageable set of suppliers and instrumentation that can address their specific analysis, characterization and monitoring needs. Table 4-1 contains the vendor input form being used to collect data from commercial vendors.

In addition to the CMST-CP Internet guide, other compilations of technologies for characterization and monitoring are available in printed or electronic form. The EPA has published a report on subsurface characterization and monitoring techniques[7] and electronically published a database on innovative field analytical and characterization technologies named Vendor FACTS[8]. The DOE recently contracted the preparation of "The Products and Services Directory for Commercial Environmental Cleanup" which also contains descriptions of commercial characterization and monitoring technologies[9]

[7] Subsurface Characterization and Monitoring Techniques, A Desk Reference Guide, Vol I: Solids and Ground Water, Vol. II: The Vadose Zone, Field Screening and Analytical Methods, EPA/R-93-003a & EPA/R-93-003b, May 1993.
[8] Vendor Field Analytical and Characterization Technologies, electronic version available as files vfdisk1.zip and vfdisk2.zip at EPA CLU-IN BBS, 301 589-8366 or at anonymous ftp://cmstsrv.ameslab.gov/public/
[9] "The Products and Services Directory for Commercial Environmental Cleanup, prepared by Rust Geotech, DOE/ID/12584-230, GJPO-120, Nov. 1995.

Table 4-1
Vendor Input Form

Vendor Input form *DOE/ EM/ CMST-CP*
Field Instrumentation & Sensors for Environmental Characterization & Monitoring

Company
Product category
Product name
Application Information
Title: typed in descriptive response

Measurement: What was measured?

specific analyte	organic	inorganic	special class	physical property
not applicable	not applicable	not applicable	not applicable	not applicable
EPA list of	VOC	metals	pyrophoric	radioactivity
regulated	SVOC	radionuclides	explosives	viscosity
chemicals	PCB	cyanides	organometallic	density
...	...	...	...	...
other	other	other	other	other

Sample Media / Matrix: What was the sample?

solid	liquid	gas	mixture
not applicable	not applicable	not applicable	not applicable
soil	water	stack	sludge
sediment	nonaqueous	soil gas	drum contents
...	...	...	...
other	other	other	other

Range: At what levels were measurements made (units)? ____________
Site: At what type of site were measurements made? ____________
Waste Source: Is the type of contamination source known? ____________
Implementation Constraints: How small? How portable? ____________
Sample Imposed Restrictions: Hazards? Homogeneous? ____________
Minimum Detectable Limits (MDL): analyte:level
typed in response
Interferences: analyte:interferant (level)
typed in response
Data Use: For what purpose was the data used? ____________
Data Quality: What was the type of data quality? ____________
Regulatory Drivers: Were there any?

Comments: references and additional information
typed in response
Web page URL reference(s): ____________

Market Study Survey of Technologies. Using the methodology of interviews and secondary research discussed earlier in this report, the Unimar Group market study identified four major categories of field instrumentation currently used for environmental characterization and monitoring. these categories were:

- Portable Gas Chromatographs
- Photoionization Detectors / Flame Ionization Detectors
- X-Ray Fluorescence Analyzers
- Immunoassay Kits

The uses of the instruments in these categories are described in the market study report (Appendix A). A number of additional commercial technologies were not described in interviews but were identified in secondary research. These other technologies also are described in the market study report and include

- Electrochemical Sensors
- Fourier Transform Infrared
- Fiber Optic Sensors

The description of the current technologies found in the market study is, by necessity, brief. To expand these descriptions considerable discussions of technologies were held at the Workshop as described in the next section.

Workshop Discussion of Technologies

On the final day of the workshop the participants were divided into workgroups to discuss technologies in seven different classifications as follows:

Fiber & Optical Waveguide Sensors	Field Deployable Instrumentation
Optical Instrumentation	Field Deployable Instrumentation - Subsurface
Electrochemical Sensors	Immunosensors
Piezoelectric Mass Sensors	

The participants in each group were asked to consider which high priority needs could be addressed by the technologies covered by their workgroup. For the relevant needs the workgroups were requested to:

- Assess technical specifications required to satisfy each need.
- Estimate cost savings benefit to customer over 10 yrs. ($ amount)
- Estimate probability of technical development success (%).
- Estimate investment and time required to bring product to market. (total $, total yrs)
- Estimate market size for product. (10 yr, total $) (List any assumptions made)

As in the case of needs discussions, each discussion group prepared outline summaries of their discussions, and a discussion leader presented the group's conclusions to the workshop as a whole.

The summaries of the workgroups did not include all the information requested, especially market size estimates, because the participants did not have or could not share some of the desired information. However, good descriptions of baseline technologies, emerging technologies and technical needs were obtained. For the purpose of this report, the workgroup discussion leaders agreed to write up summaries of their groups discussions prefaced with background information about the technologies addressed by the workgroup. These summaries are included in the following subsections.

Piezoelectric Mass Sensors by Gregory Frye, Sandia National Laboratory

Participants: Frederick Anvia, Femtometrics; Eddie Christy, METC; Colin Cumming, Nomadics; Carl Freeman, Sensor R&D Crop.; Brent Horine, Sawtek; Gus Manning, Assay Technology

Background. (by Glenn Bastiaans, Ames Laboratory) Piezoelectric devices are sensors which transmit acoustic waves through a solid substrate and which are extremely sensitive to the adherence of mass to the surface of the device. Several types of acoustic piezoelectric devices are used as sensors. These types include quartz crystal microbalances (QCMs), which are bulk acoustic wave resonators, surface acoustic waveguides (SAWs), and others. These devices have the advantages that they can be fabricated in relatively small sizes (dimensions as small as a few mm) and are inexpensive to manufacture.

For all of these devices, two independent device responses, signal phase change and wave attenuation, can be simultaneously monitored. The responses can be used to quantitate the amount of material which adheres to or is sorbed to the sensor surface. If deployed in a liquid, some sensors will also produce response information which is a function of the density and viscosity of that liquid.

To obtain sensors which only respond to specific substances, samples must be separated into individual components before exposure to the sensor or coatings must be placed on sensors to cause the surface sorption of only selected substances. Current technology development efforts are focused on the improvement of selective sensor coatings, the design of sensor array systems, the development of pattern recognition methods, temperature compensation methods, and signal to noise enhancement techniques.

Significant Needs That Piezoelectric Sensors Can Meet. The group initially discussed how to look at the needs and decided to focus on key contaminant groups, such as organics, RCRA metals, and radioactive metals, and consider the matrices (air, water, soil) and the issue of in situ as subtopics for each contaminant group. In discussions of the key strengths and weaknesses of piezoelectric sensors, it was decided that they could be made small, portable, and rugged so that for any given need, in situ deployment was a possibility and an area where these sensors had an advantage. Since these sensors rely on detecting chemical species sorbed in a coating on the surface, they are not capable of remote detection (defined by the group as non-contact and distant detection such as in long pathlength optical techniques); however, they could be configured to operate remotely with telemetry for transmission of the data to a central receiver (e.g., boundary monitoring).

Regarding matrices, all piezoelectric sensors are capable of monitoring chemicals in air and several are capable of direct liquid contact and detection of species in liquids. However, in order to perform analysis of soil or other solid materials (e.g., solid wastes, concrete, metals), the need for chemical to enter the coating to be detected requires a sampling front end, such as a purge-and-trap system, to transfer the species to be detected into an air or water sample. For organics, this is often easy to accomplish; however, some of the needs are unlikely to be impacted since the species may be hard to separate from the matrix (e.g., radioactive metals in metal, concrete, and solids). It was also discussed that for liquids, if the species could be partitioned out into the vapor phase (e.g., headspace or purge-and trap analysis for volatile organics), this would generally be preferred over direct detection in water due to the challenge of maintaining the sensor free of surface contamination and the issue of compensating for changes in viscosity and density of the contacting liquid (this sensitivity can be used to make in situ viscosity measurements using these devices -- since this need was not identified, this topic was not discussed in detail).

Discussion also focused on the best applications for piezoelectric sensors and it was decided that with sensor array capabilities and selective coating chemistry, monitoring systems to identify and quantify species in simple mixtures were a realistic possibility. However, it was felt that the capabilities would not be sufficient for detailed characterization of complex mixtures, such as is typically performed for EPA certified site characterization using laboratory instrumentation. This was based on excluding systems that include a chromatographic separation stage, such as the Amerasia system that uses a piezoelectric detector to perform fast gas chromatographic analyses. The group felt these systems should be considered in the gas chromatography technology area rather than the piezoelectric sensors area. Thus, the best application was felt to be monitoring since for many monitoring applications, only a few compounds, that are typically known ahead of time, are of interest. Monitoring includes ambient air, workplace, and personnel monitoring as well as exhaust stack and waste and process stream monitoring. It was decided that the ability to identify and quantify species would be an advantage over simple detectors (e.g., PIDs) for monitoring applications while the small size, low cost, fast response, and ease of use would be an advantage over more complex instruments (e.g., GC, FTIR, MS). The capabilities would also be well suited to field screening but the advantages, though still there, are not as strong when comparing with PIDs and other nonspecific detectors. Since a big cost is analysis of "clean" samples, a speciating field screening tool might be able to provide significant cost savings in minimizing off-site analyses.

Organic Contaminants: It was felt that the best application of piezoelectric sensors was for organic detection since: (1) coatings for sensitive and selective detection have been demonstrated, (2) there are many air/vapor monitoring needs, and (3) for liquids and soils, most organics can be volatilized for detection in the vapor phase (the only method for soil and felt to be the best for liquids). Detection of VOCs, SVOCs, and a subset of HAPS is possible. Generally, detection levels would be low ppm for direct analysis and low to mid ppb using an adsorbent preconcentrator to collect the chemical and thermally desorb it into a concentrated sample plug. Similar detection levels expected in air, water and soil. An analysis was performed to estimate the return on investment over the next 10 years. It was estimated that the total environmental laboratory and field analysis would be 10 billion over the next ten years. The following assumptions were used: (1) 50% of this was organics (they are the largest class of contaminants), (2) a third (33%) of the available needs could be impacted by piezoelectric sensors, (3) a 30% market penetration, (3) a 50% cost savings where piezoelectric sensors were employed, (4) an 80% estimated probability of success, and (5) a 5M investment needed to bring the technology to market. These assumptions give a return on investment of 40 ($200M/$5M).

RCRA Metals (aqueous/gaseous): The second best application for piezoelectric sensors was decided to be RCRA metals in water or air (for volatile metals). Single species, mercury (Hg), has been demonstrated and is being developed. Coatings for additional RCRA metals could be developed. By merging with electrochemical methods, can monitor/detect various other RCRA metals. A return on investment of 10 ($50M/$5M) was calculated using the same assumptions except only 25% of total was assumed to be for RCRA metals and a 40% estimated probability of success was used.

Radioactive Metals: It was felt that piezoelectric sensors would not be competitive for radioactive species.

Inorganic Gases and Auto Emissions: Work has been done using chemeresistive layers to detect combustion gases with an order of magnitude increase in sensitivity observed compared with using these layers with direct electrical probing. This may be applicable to combustion process control, CEMs and stack sensors, and automotive emissions depending on costs. It was felt that this was more important for process control and pollution prevention and less important for environmental remediation.

Fiber & Optical Waveguide Sensors

Fiber and Waveguide Sensors: Environmental Assay Market Awaits New Products.
by Kish Goswami, Physical Optics Corp.

An explosive growth in the applications and sales of fiber optic sensors was predicted in a 1993 Frost & Sullivan Market Intelligence study[10]. That study predicted $1.12 billion market by 1999 representing a compound annual growth rate of 36.6% starting from worldwide $126 million market in 1992. A separate study, however, has substantially scaled down the projection of worldwide market to $177 million in 1998. Clearly, the fiber and waveguide sensors are still at their infancy compared to conventional sensors, and they represent wave of the future.

Waveguide Sensors

Waveguides are thin cylinders or flat segment of glass or plastic that transmit light by total internal reflection. Developed originally for telecommunications and optical computing applications, they have found another application in the analytical field as chemical and physical sensors. Optical fibers are a subset of waveguides. Fiber and waveguide sensors represent a dramatic shift from conventional sensors because fiber alternatives are potentially superior in terms of real time, in situ application in remote locations. Furthermore, these sensors represent a breakthrough in weight, size, immunity to electromagnetic interference, sensitivity, and power requirement.

It is possible to use waveguides for just delivering a flux of photons to an analyte. For optical fibers, the photons emerge out of the fiber at the distal end where absorbance, luminescence, and scattering are caused by analytes. The modified light beam can be collected by the same fiber or by different fibers in a bundle. This approach resembles direct spectroscopy with spectrometers. Instead of using the fiber tip, the side of an optical fiber can also be used. When the cladding of a fiber is removed, part of the guided light leaks out and interacts with analytes in the surrounding medium. This evanescent wave interaction offers the possibility of sensing over a large surface area. Waveguide chemical sensors employ chemical indicators for the sensitive and specific detection of analyte. The indicator can be incorporated on the tip or side of an optical fiber, or on the face of a flat waveguide.

The potential applications of optical fiber in chemical analysis have long been recognized and were reported as early as 1969[11]. Although viable products lack in the marketplace, a tremendous amount of literature have been published by the academic community on fiber optic sensors. This interest can be attributed to substantial improvements in the fiber quality, cost and wider availability in the market. Using a fiber sensor, concentrations of volatile and toxic chemicals can be measured anywhere along the path of a fiber. A typical fiber sensor includes an optoelectronic package, optical fiber, and the sensor. The transduction mechanism involves change in a parameter of the guided light such as its intensity, lifetime, or phase.

[10] Photonics Spectra, July 1993, page 49.
[11] Crum, J. K., Anal. Chem. 41, 26A, 1969.

Significant Needs That Waveguide Sensors Can Meet

Of all the technologies discussed in the workshop, waveguide sensor appears to be most versatile for:

- Subsurface Characterization
- Waste Characterization
- Process Monitoring
- Effluent Monitoring
- Contaminant Monitoring, and
- Air Quality Monitoring

Currently, site characterization and monitoring are mostly achieved by collecting representative samples, and analyzing them in analytical laboratories away from the sites. In some cases, analyses are done in a mobile laboratory at the site. Still, samples need to be collected. In addition to being expensive, sampling methods may hamper the integrity of the samples, and may also perturb the sampling zone. Table 4-1 shows some of the field-usable baseline technologies, and their analytical applications.

TABLE 4-1
Baseline Technologies for Field Characterization and Monitoring

TECHNOLOGIES	APPLICATION
Gas Chromatography	Organics (volatile and semi-volatile) in air, water, and soil. Air quality monitoring.
Photoionization/Flame ionization	Organics in air.
X-Ray Fluorescence	Radionuclides and metals in water, and soil.
Immunoassay	Organics in water, and soil
Electrochemical Detection	Ions in water; gases in air
Infrared Absorption	Organics in air, gases in air
Fiber Optic Technology	Organics in water, and soil vapor

Numerous optical sensing methodologies described in the past await their commercial application. Cost and performance are important issues. The environmental community is tuned to high performance instruments such as GC, GC-MS, AA, and ICP. Customers of fiber and waveguide sensors need to be educated. This is true for any new technology undergoing market development. Customers also expects low cost, field deployable fiber optic sensor systems because this expectation has been reinforced for many years through numerous publications.

The fiber and optical waveguide sensors workgroup prioritized the needs that the technology can fulfill. The factors considered were:

- Uniqueness of the technology

- Commercial potential
- Cost savings impact over ten year period

The top seven prioritized needs are:

- Organics in soil (soil gas)
- Organics in water
- Organics in headspace
- Organics/RCRA metals in water
- Air quality monitoring
- Inorganics in water, and
- Inorganics in soil

Capabilities and Benefits of Fiber and Optical Waveguide Sensors

Environmental instrument manufactures have historically been tied to the fortunes of their traditional customers – the analytical laboratory. With that end market now mature, still adjusting to overcapacity, buyers are demanding instruments that will deliver cost-savings, and efficiencies. Traditional analytical techniques do not allow low cost, real time, and in situ measurements of analytes. This is where optical waveguide sensors will make the difference. Coupling analytical technologies to a cone penetrometer offers a cost-effective, and efficient means of obtaining contaminant levels for subsurface characterization and monitoring. Waveguide sensors will meet this need also.

Regulatory controls and environmental awareness are propelling more testing and monitoring. These activities are unlikely to diminish. To bring down the cost, portable field-based devices for continuous monitoring have been the focus of innovation. Industry leader Perkin- Elmer (Norwalk, CT) has recognized this need as evidenced by its $20 million purchase of Photovac (Markham, Ontario), manufacturer of portable gas analyzers. Instead of abandoning established technologies, large instrument manufacturers are spending R&D resources in miniaturizing lab instruments. However, despite the promise, developers of fiber and waveguide sensors do not yet have strong funding support outside the federal government.

Under the current state of development, fiber and optical waveguide sensors will not be in a position to replace big-ticket lab instruments. Traditional lab instruments can detect analytes with high accuracy, sensitivity, and specificity. Use of waveguide sensors, through preliminary screening, will benefit customers by reducing the number of samples for lab tests. Waveguide sensors will also save unnecessary sampling and lab testing by indicating trends during site monitoring.

Optical Instrumentation

Optical instruments can quantify the concentration of substances present in a sample by measuring the degree of electromagnetic radiation which is emitted, absorbed, fluoresced, or scattered by the substance. Indications of the identity of the substance can be obtained by determining the wavelengths of radiation which interact it. The definition of “optical” methods generally encompasses interactions with radiation having wavelengths that range from the infrared to the vacuum ultraviolet (uv), although microwave, x-ray, and gamma spectroscopic techniques may have significant applications as well.

This workgroup was led by William Walter, AIL Systems, and primarily discussed optical instrumentation which did not use optical waveguides and which utilized wavelengths over the infrared to vacuum uv range. Upon examination of the priority needs of Table 3-2, it was observed that most of these needs could be met by optical spectroscopy, particularly the measurement of organics in soil and in air. It was concluded that the media form of the sample influenced how well optical methods could detect and quantitate analytes as follows:

Sample Media	Suitability of Application
Air	Excellent application
Surface	Good application
in H_2O	Poorer application

The workgroup discussed several optical methods which show promise for field applications and evaluated them in terms of state of commercial development and special applications These methods and the workgroup comments are listed in Table 4-2.

It was also noted that x-ray, gamma, and neutron spectroscopy have the potential to be effective tools for the examination of waste containers such as drums and boxes.

In the discussion following the presentation of the results of this workgroup, it was noted that an additional promising development in this area was instrumentation that could spatially map optical absorption in the air over the infrared and visible regions of the spectrum yielding an indication of the dispersion of chemicals at a sample site.

Table 4-2
Optical Devices

Optical Method	Commercial Availability	Comments
open-path FTIR	Commercially Available	A few commercial suppliers exist; applications appear to be expanding
Differential Absorption LIDAR	Under Development	A laser light scattering measurement method that allows remote sensing and gives distance range to sampled substance
UV Differential Optical Absorption Spectroscopy	Commercially Available	UV absorption does not suffer interferences from water and so is more suitable for water based samples
laser ablation	Under Development	Suitable for solid sampling
laser induced breakdown spectroscopy (LIBS)	Commercially Available	Emission spectroscopic method suitable for solid sampling. A commercial version was field tested for the measurement of heavy metals in soils.
laser spark spectroscopy (LASS)	Under Development	Emission spectroscopic method suitable for solid sampling.
Raman	Under Development	A scattering method which has shown some promise in the laboratory.
visible absorption	Under Development	A method which can detect radionuclides which have a 5f optical transition (absorbance in the visible region of the spectrum)

<u>Electrochemical Sensors</u> by Joseph Wang, New Mexico State University and Joseph Stetter, Transducer Research Inc.

The introduction to this technology area is provided in the form a a recent EPA report authored by Joseph Wang. A summary of the Workgroup discussion is provided by Joseph Stetter.

Introduction.

Electrochemical Sensors For Environmental Monitoring: A Review Of Recent Technology
JOSEPH WANG Department of Chemistry and Biochemistry, New Mexico State University, Las Cruces, New Mexico 88003
Written in response to Solicitation No. LV-94-012
Project Officer ; Kim Rogers, EMSL - U.S. EPA, P.O. Box 93478, Las Vegas, NV 89139-3478
Included by permission of authors and U. S. EPA.: Report No. EPA/540/R-95/507

Electroanalytical chemistry can play a very important role in the protection of our environment. In particular, electrochemical sensors and detectors are very attractive for on-site monitoring of priority pollutants, as well as for addressing other environmental needs. Such devices satisfy many of the requirements for on-site environmental analysis. They are inherently sensitive and selective towards electroactive species, fast and accurate, compact, portable and inexpensive. Such capabilities have already made a significant impact on decentralized clinical analysis. Yet, despite their great potential for environmental monitoring, broad applications of electrochemical sensors for pollution control are still in their infancy.

Several electrochemical devices, such as pH- or oxygen electrodes, have been used routinely for years in environmental analysis. Recent advances in electrochemical sensor technology will certainly expand the scope of these devices towards a wide range of organic and inorganic contaminants and will facilitate their role in field analysis. These advances include the introduction of modified- or ultramicroelectrodes, the design of highly selective chemical or biological recognition layers, of molecular devices or sensor arrays, and developments in the areas of microfabrication, computerized instrumentation and flow detectors.

The EPA's Office of Research and Development is currently pursuing the development of environmental monitoring technologies which can expedite the characterization of hazardous waste sites in the U.S. Relevant to this objective, is the review and evaluation of currently reported field analytical technologies. The objective of this report is to describe the principles, major requirements, prospects, limitations, and recent applications of electrochemical sensors for monitoring ground or surface waters. It is not a comprehensive review of these topics, but rather focuses on the most important advances and recently reported devices which hold great promise for on-site water analysis.

Principles. The purpose of a chemical sensor is to provide real-time reliable information about the chemical composition of its surrounding environment. Ideally, such a device is capable of responding continuously and reversibly and does not perturb the sample. Such devices consist of a transduction element covered with a biological or chemical recognition layer. In the case of electrochemical sensors, the analytical information is obtained from the electrical signal that results from the interaction of the target analyte and the recognition layer. Different electrochemical devices can be used for the task of environmental monitoring (depending on the nature of the analyte, the character of the sample matrix, and sensitivity or selectivity requirements). Most of these devices fall into two major categories (in accordance to the nature of the electrical signal): amperometric and potentiometric.

Amperometric sensors are based on the detection of electroactive species involved in the chemical or biological recognition process. The signal transduction process is accomplished by controlling the potential of the working electrode at a fixed value (relative to a reference electrode) and monitoring the current as a function of time. The applied potential serves as the driving force for the electron transfer reaction of the electroactive species. The resulting current is a direct measure of the rate of the electron transfer reaction. It is thus reflecting the rate of the recognition event, and is proportional to the concentration of the target analyte.

In potentiometric sensors, the analytical information is obtained by converting the recognition process into a potential signal, which is proportional (in a logarithmic fashion) to the concentration (activity) of species generated or consumed in the recognition event. Such devices rely on the use of ion selective electrodes for obtaining the potential signal. A permselective ion-conductive membrane (placed at the tip of the electrode) is designed to yield a potential signal that is primarily due to the target ion. Such response is measured under conditions of essentially zero current. Potentiometric sensors are very attractive for field operations because of their high selectivity, simplicity and low cost. They are, however, less sensitive and often slower than their amperometric counterparts. In the past, potentiometric devices have been more widely used, but the increasing amount of research on amperometric probes should gradually shift this balance. Detailed theoretical discussion on amperometric and potentiometric measurements are available in many textbooks and reference works.[1-5]

Electrochemical Biosensors. The remarkable specificity of biological recognition processes has led to the development of highly selective biosensing devices. Electrochemical biosensors hold a leading position among the bioprobes currently available and hold great promise for the task of environmental monitoring. Such devices consist of two components: a biological entity that recognizes the target analyte and the electrode transducer that translates the biorecognition event into a useful electrical signal. A general schematic diagram for the operation of electrochemical biosensors is shown in Figure 4-1. A great variety of schemes for implementing the electrochemical biosensing approach, based on different combinations of biocomponents and electrode transducers have been suggested. These rely on the immobilization of enzymes, antibodies, receptors or whole cells onto amperometric or potentiometric electrodes. Fundamental aspects of these devices have been reviewed in the literature.[6-8]

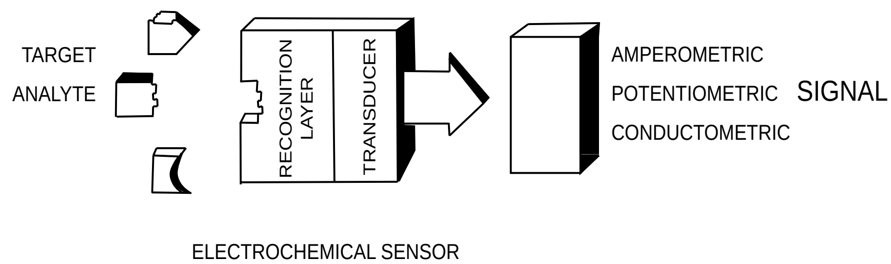

Figure 4-1. Electrochemical biosensors: biorecognition and signal transduction

Enzyme electrodes have the longest tradition in the field of biosensors. Such devices are usually prepared by attaching an enzyme layer to the electrode surface, which monitors changes occurring as a result of the biocatalytic reaction amperometrically or potentiometrically. Amperometric enzyme electrodes rely on the biocatalytic generation or consumption of electroactive species. A large number of hydrogen-peroxide generating oxidases and NAD^+-dependent dehydrogenases have been particularly useful for the measurement of a wide range of substrates The liberated peroxide or NADH species can be readily detected at relatively modest potentials (0.5-0.8V vs. Ag/AgCl), depending upon the working electrode material. Lowering of these detection potentials is desired for minimizing interferences from coexisting electroactive species. Potentiometric enzyme electrodes rely on the use of ion- or gas-selective electrode transducers, and thus allow the determination of substrates whose biocatalytic reaction results in local pH changes or the formation or consumption of ions or gas (e.g. NH_4^+ or CO_2). The resulting potential signal thus depends on the logarithm of the substrate concentration. Proper functioning of enzyme electrodes is greatly dependent on the immobilization procedure.

The design of enzyme electrodes is such that the current or potential measured is proportional to the rate limiting step in the overall reaction. For reactions limited by the Michaelis-Menten kinetics, a leveling off of calibration curves is expected at high substrate concentrations. Mass-transport limiting membranes can be used to greatly extend the linear range. This will also lead to a slower response. The signal may be dependent also upon the pH of the water sample or its heavy-metal content that affect the enzymatic activity. Attention should be given also to the long-term stability of these devices, due to the limited thermostability of the biocatalytic layer. Improved immobilization and use of thermophilic or 'synthetic' enzymes should be useful for extending the lifetime of enzyme electrodes (particularly in connection with field applications). Mass producible, disposable enzyme electrodes can be readily fabricated (as common for clinical self-testing of blood glucose), and used as 'one-shot' throwaway devices.

Several enzyme electrodes have already proven useful for the task of environmental monitoring. For example, several groups reported on highly sensitive amperometric biosensors for phenolic compounds.[9-15] Such devices rely on the immobilization of tyrosinase (polyphenol oxidase) onto carbon- or platinum transducers, and the low potential detection of the liberated quinone product

(Figure 4-2). Assays of industrial wastes or natural water have been documented,[12-14] including possible remote phenol sensing[13] and single-use on-site sensing.[14,15] Similarly, low potential biosensing of organic peroxides or hydrogen peroxides can be accomplished at peroxidase-modified electrodes.[16,17] "Class-selective" enzyme electrodes, based on tyrosinase or peroxidase, can be used for semi-quantitative field screening. They can also be used as detectors for liquid chromatography, hence providing quantitation of the individual substrates.[18] The organic-phase activity of these enzymes should be useful not only for chromatographic separations, but also in connection with rapid solvent extraction procedures. Other enzymes, such as sulfite oxidase, nitrate reductase, nitrilase, alcohol dehydrogenase, or formaldehyde dehydrogenase have been employed for electrochemical biosensing of environmentally-relevant species such as sulfite,[19] nitrate,[20] organonitriles,[21] alcohols,[22] or formaldehyde,[23] respectively. Most of the above devices offer low (micromolar) detection limit, good precision (RSD = 1-3%) and fast (30-60 sec.) response.

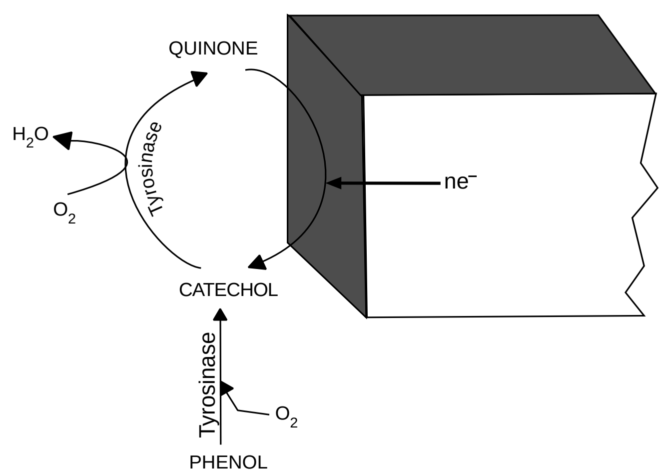

Figure 4-2 Enzyme (tyrosinase) electrode for monitoring phenolic compounds

In addition to substrate monitoring, it is possible to employ enzyme electrodes for measuring various toxins (via the perturbation/modulation of the enzyme activity). For example, the inhibition of enzymes, such as cholinesterase, tyrosinase, or peroxidase, has led to useful biosensors for organophosphates and carbamates pesticides,[24] cyanide,[25] or toxic metals.[26,27] The resulting (inhibition) plots thus reflect the enzyme inhibition kinetics. Such enzyme inhibition devices may thus be useful as early warning poison detectors. Improved specificity may be achieved by designing multi-enzyme arrays that offer a "fingerprint" pattern of the individual inhibitors. Analogous detection of benzene or herbicide contaminations and of anionic surfactants can be accomplished by immobilizing whole cells onto electrodes and monitoring the modulation in the microbial activity.[28,29,30] Another environmentally important microbial sensor offers rapid estimate of BOD (biochemical oxygen demand), hence replacing the long (5 day) conventional BOD test.[31] The use of whole cells (instead of isolated enzymes) can increase the sensor stability and allows regeneration of the bioactivity (via immersion in a nutrient media).

Other whole cell electrodes, relying on plant tissues (such as mushroom or horseradish) have been used for detecting phenolic and peroxide substrates (of their tyrosinase and peroxidase enzymes). While offering prolonged lifetimes, such tissue electrodes may suffer from side reactions due to the coexistence of several enzymes.

Affinity electrochemical biosensors, employing natural binding molecules as the recognition element should also play a growing role in future environmental monitoring. In this case the recognition process is governed primarily by the shape and size of the receptor pocket and the analyte of interest. Particularly promising are electrochemical immunosensors due to the inherent specificity of antibody-antigen reactions.[32] Disposable immunoprobes based on mediated electrochemistry have been developed.[33] In addition to immunosensors, the environmental arena may benefit from the production of electrochemical immunoassay test kits. Such assays commonly rely on labelling the antigen with an electroactive tag (Figure 4-3A), or with an enzyme that acts on a substrate and liberates an electroactive product (Figure 4-3B). A wide variety of enzymes are suitable (peroxidase, alkaline phosphatase, etc.), and there is also a wide choice of substrates for these enzymes. New test kits, developed for the clinical market, may be readily adapted for environmental monitoring. Other promising concepts are based on specific binding between membrane-embedded receptors and target analytes[34] or the hybridization of electroactive markers by surfacebound DNA.[35] Amperometric or potentiometric transducers are useful to follow these binding events. Genetic engineering technology is currently being explored for designing binding molecules for target analytes.

Chemically Modified Electrodes for Environmental Monitoring. Chemical layers can also be used for imparting a high degree of selectivity to electrochemical transducers. While conventional amperometric electrodes serve mainly for carrying the electrical current, powerful sensing devices can be designed by a deliberate modification of their surfaces. Basically, the modification of an electrode involves immobilization (on its surface) of reagents that change the electrochemical characteristics of the bare surface. Inclusion of reagents within the electrode matrix (e.g. carbon paste) is another attractive approach for modifying electrodes. Such manipulation of the mole-cular composition of the electrode thus allows one to tailor the response to meet specific sensing needs. The new “mercury-free” surfaces address also growing concerns associated with field applications of the classical mercury drop electrode. Theoretical details on modified electrodes can be found in several reviews.[36-38]

While sensors based on modified electrodes are still in the early stages of their lifetime, such preparation of structured interfaces holds great promise for the task of environmental monitoring. There are different directions by which the resulting modified electrodes can benefit environmental analysis, including acceleration of electron-transfer reactions, preferential accumulation or permselective transport.

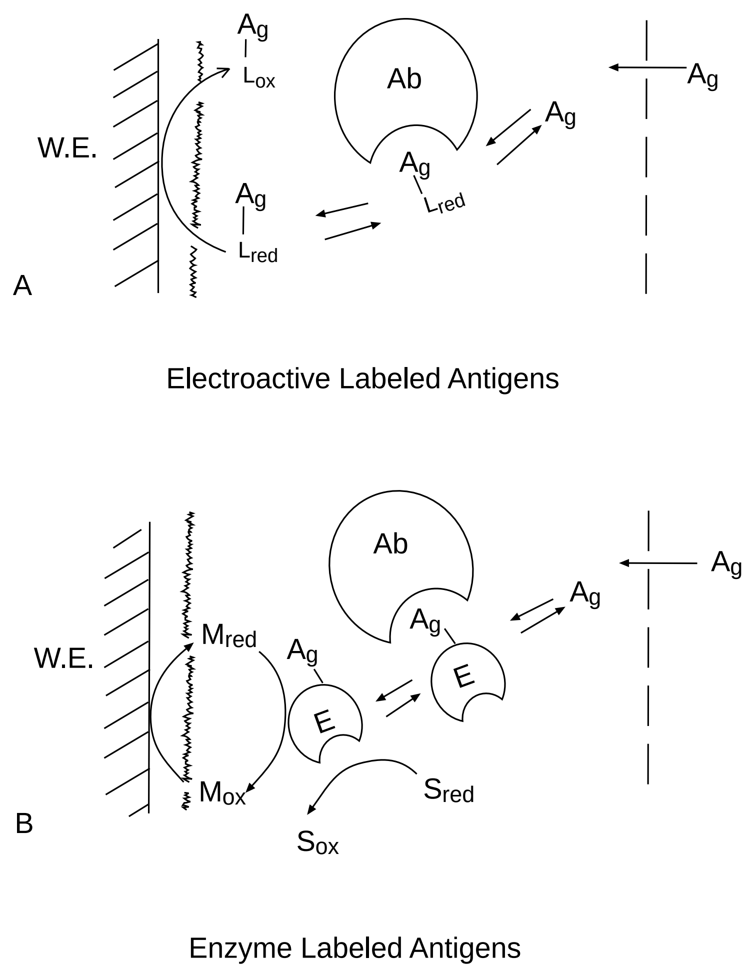

Figure 4-3 Amperometric immunosensor based electroactive-(A) and enzyme (B) tagged antigen

Electrocatalysis involves an electron transfer mediation between the target analyte and the surface by an immobilized catalyst (Figure 4-4). Such catalytic action results in faster electrode reactions at lower operating potentials. Various catalytic surfaces have thus been successfully employed for facilitating the detection of environmentally-relevant analytes (with otherwise slow electron-transfer kinetics). These include the electrocatalytic determination of hydrazines[39] or nitrosamines[40] at electrodes coated with mixed-valent ruthenium films, monitoring of aliphatic aldehydes at palladium-modified carbon paste,[41] sensing of nitrite at a glassy carbon electrode coated with an osmium-based redox polymer,[42] of nitrate at a copper modified screen printed carbon electrode,[43] monitoring of organic peroxides at cobalt-phthalocyanine containing carbon pastes,[44] and of hydrogen peroxide at a copper heptacyano-nitrosylferrate-coated electrode.[45]

Preconcentrating modified electrodes can also be useful for environmental sensing. In this case an immobilized reagent (e.g. ligand, ion-exchanger) offers preferential uptake of target analytes. This approach enjoys high sensitivity because it is a preconcentration procedure. A second major advantage lies in the added dimension of selectivity, which is provided by the chemical requirement of the modifier-analyte interactions. Such improvements have been documented for the measurement of nickel, mercury, or aluminum ions at dimethylglyoxine,[46] crown-ether,[47] or alizarin[48] containing carbon pastes, respectively, monitoring of nitrite, chromium, or uranyl ions at ion-exchanger modified electrodes,[49-51] and of copper at an algaemodified electrode.[52] Covalent reactions can be used for analogous collection/determination of organic analytes, e.g. monitoring of aromatic aldehydes at amine-containing carbon pastes.[53] Routine environmental applications of these preconcentrating electrodes would require attention to competition for the surface site and the regeneration of an 'analyte-free' surface.

Another promising avenue is to cover the sensing surface with an appropriate permselective film. Discriminative coatings based on different transport mechanisms (based on analyte size, charge, or polarity) can thus be used for addressing the limited selectivity of controlled-potential probes in complex environmental matrices. The size-exclusion sieving properties of various polymer-coated electrodes offer highly selective detection of small hydrogen peroxide or hydrazine molecules.[54, 55] In addition, surface passivation (due to adsorption of macromolecules present in natural waters) can be prevented via the protective action of these films.

More powerful sensing devices may result from the coupling of several functions (permselectivity, preconcentration or catalysis) onto the same surface. Additional advantages can be achieved by designing arrays of independent modified electrodes, each coated with a different modifier and hence tuned toward a particular group of analytes. The resulting array response offers a unique fingerprint pattern of the individual analytes, as well as multicomponent analysis (in connection with statistical, pattern-recognition procedures). Use of different permselective coatings or catalytic surfaces thus hold great promise for multiparameter pollution monitoring. The development of electrochemical sensor arrays has been reviewed recently.[56] Related to this are new molecular devices based on the coverage of interdigitated microarrays with conducting polymers.[57,58] Eventually we expect to see molecular devices in which the individual components are formed by discrete molecules. Modification of miniaturized screen-printed sensor strips can also be accomplished via the inclusion of the desired reagent (e.g. ligand, catalyst) in the ink used for the microfabrication process.

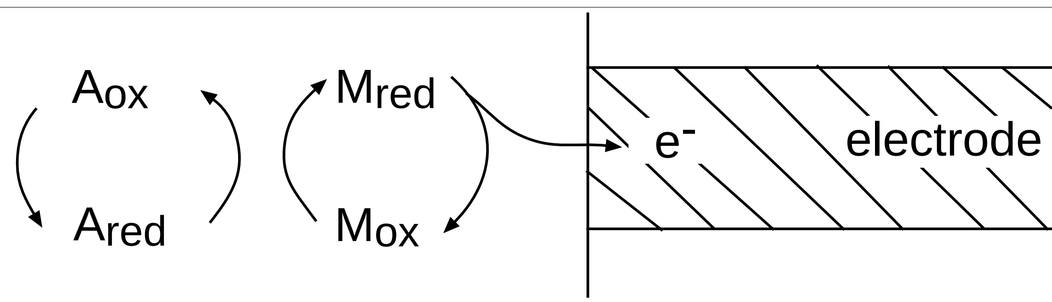

Figure 4-4 Electrocatalysis at modified electrodes; electron transfer mediated reaction between the target analyte and surface-bound catalyst

Stripping-based Metal Sensors. The most sensitive electroanalytical technique, stripping analysis, is highly suitable for the task of field monitoring of toxic metals. The remarkable sensitivity of stripping analysis is attributed to its preconcentration step, in which trace metals are accumulated onto the working electrode. This step is followed by the stripping (measurement) step, in which the metals are "stripped" away from the electrode during an appropriate potential scan. About 30 metals can thus be determined by using electrolytic (reductive) deposition or adsorptive accumulation of a suitable complex onto the electrode surface (Figure 4-5). Stripping electrodes thus represent a unique type of chemical sensors, where the recognition (accumulation) and transduction (stripping) processes are temporally resolved. Short accumulation times (of 3-5 min) are thus sufficient for convenient quantitation down to the sub-ppb level, with shorter periods (1-2 min) allowing measurements of ppb and sub-ppb concentrations. The timeconsuming deaeration step has been eliminated by using modern stripping modes (e.g. potentiometric or square-wave stripping), that are not prone to oxygen interferences. Stripping analysis can provide useful information on the total metal content, as well as characterization of its chemical form (e.g. oxidation state, labile fraction, etc.).[59] Field measurements of chromium(VI) represent one such example.[60,61] Overlapping peaks, formation of intermetallic compounds and surfactant adsorption represent the most common problems in stripping analysis.

Various advances in stripping analysis should accelerate the realization of on-site environmental testing of toxic metals. New sensor technology has thus replaced the traditional laboratory-based mercury electrodes and associated cumbersome operation (oxygen removal, solution stirring, cell cleaning, etc.). Of particular significance are new stripping-based tools, such as automated flow systems for continuous on-line monitoring,[62-64] disposable screen-printed stripping electrodes for single-use field applications,[65] or remote/submersible devices for down-hole well monitoring or unattended operation.[66,67] Portable and compact (hand-held), battery-operated stripping analyzers are currently being commercialized for controlling these field-deployable devices. In addition to providing on-site realtime information, such in-situ devices should minimize errors (due to contamination or loss) inherent to trace metal measurement in a centralized laboratory. Stripping analysis has been extensively used by marine chemists on board ships for numerous oceanographic surveys.[62] Relevant examples of environmental applications of stripping analysis are given in Table 4-3.

In addition to trace metal pollutants, it is possible to employ new adsorptive stripping procedures for measuring low levels of organic contaminants that display surface-active properties (e.g. detergents, oil components). However, due to competitive adsorption such schemes usually require a prior separation step. Another version of stripping analysis, cathodic stripping voltammetry, can be used for measuring environmentally-relevant anions (e.g. S^{-2}, I^-, Br^-) or sulfur- or chlorine-containing pollutants (e.g. pesticides) following their oxidative deposition onto the working electrode. Additional background information on stripping analysis and its environmental opportunities can be found in various books or reviews.[77-80]

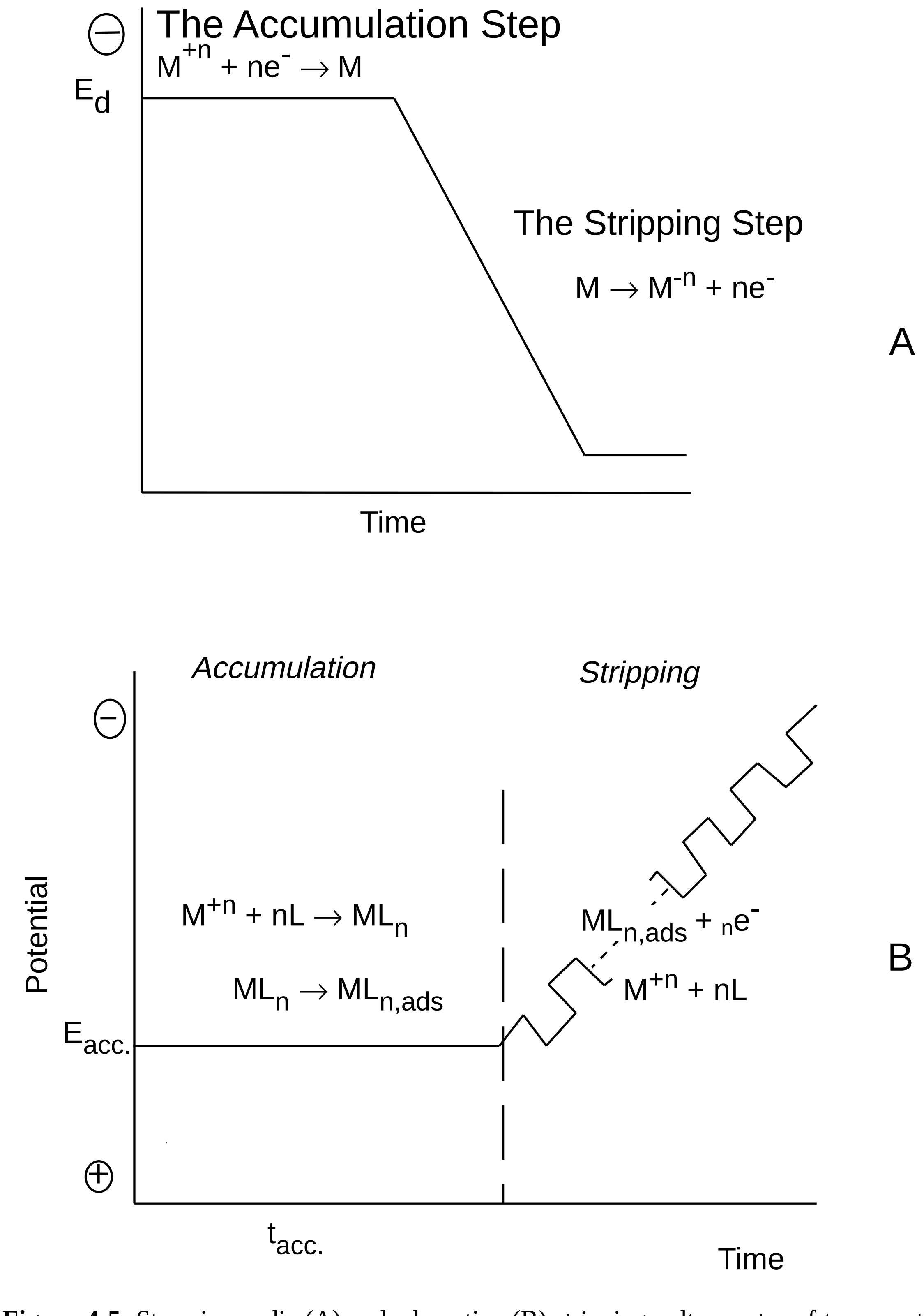

Figure 4-5 Steps in anodic (A) and adsorptive (B) stripping voltammetry of trace metals, based on electrolytic and adsorptive accumulation, respectively, of target metal analytes

Table 4-3.
Typical Environmental Applications of Stripping Analysis

Trace Metal	Matrix	Electrode	Stripping Mode	Ref.
As	Natural waters	Gold	Differential pulse	68
Cd	Lakes and Oceans	Mercury film	Differential pulse	65
				69
Cr	Seawater	Mercury drop	Adsorptive	61
	Sediments			60
Cu	Tap water	Mercury film	Potentiometric	70
Hg	Seawater	Gold	Differential pulse	71
Mn	Natural waters	Mercury drop	Potentiometric	72
Ni	Seawater	Mercury drop	Adsorptive	73
Pb	Lakes and Oceans,	Mercury film	Differential pulse	65,
	Sediments	Mercury film	Potentiometric	69
				60
Se	River water	Gold	Potentiometric	74
Tl	Natural waters	Mercury film	Differential pulse	75
U	Groundwater	Mercury drop	Adsorptive	76
	Sediments			

Ion and Gas Selective Electrodes. Ion selective electrodes offer direct and selective detection of ionic activities in water samples. Such potentiometric devices are simple, rapid, inexpensive and compatible with on-line analysis. The inherent selectivity of these devices is attributed to highly selective interactions between the membrane material and the target ion. Depending on the nature of the membrane material used to impart the desired selectivity, ion selective electrodes can be divided into three groups: glass, solid, or liquid electrodes. Many ion selective electrodes are commercially available and routinely used in various fields.

By far the most widely used ion selective electrode is the pH electrode. This glass-membrane sensor has been used for environmental pH measurements for several decades. Its remarkable success is attributed to its outstanding analytical performance, and in particular to its extremely high selectivity for hydrogen ions, broad dynamic range, and fast and stable response. Various solid-state crystalline membrane electrodes have been shown useful for monitoring environmentally-important ions, such as F^-, Br^-, CN^-, S^{-2} or $Cu.^{+2}$[81] The calcium and nitrate ion-exchanger sensors represent environmentally useful liquid membrane electrodes. The synthetic design of macrocyclic polyether ionophores has led to liquid membrane electrodes for heavy metals, such as lead or zinc.[82] Anion selective liquid membrane electrodes have been developed in recent years for sensing of phosphate or thiocyanate. New technologies of thin film (dry-reagent) slides or semiconductor chips will certainly facilitate field monitoring of ionic analytes.[83] The principles and applications of ion selective electrodes have been reviewed.[84-86]

The rapid detection of ammonia or oxygen plays a vital role in pollution control. Gas sensing electrodes are highly selective devices for monitoring these (and other) gases. Such sensors commonly incorporate a conventional ion selective electrode, surrounded by an electrolyte solution and enclosed by a gas permeable membrane. The target gas diffuses through the membrane and reacts with the internal electrolyte, thus forming or consuming a detectable ionic species. The ammonia selective probe uses an internal pH glass electrode in connection with an ammonium chloride electrolyte. The glass electrode detects the decreased activity of protons. While most gas sensors rely on potentiometric detection, the important oxygen probe is based on covering an amperometric platinum cathode with a Teflon or silicon rubber membrane. Handheld and remote oxygen probes are available commercially.[87] Potentiometric sensors for other gases (SO_2, NO_2, HF, etc.) have been designed by using different membranes and equilibrium processes.

Conclusions. Electrochemical sensor technology is still limited in scope, and hence cannot solve all environmental monitoring needs. Yet, a vast array of electrochemical sensors have been applied in recent years for monitoring a wide range of inorganic and organic pollutants (Table 4-4). We are continuously witnessing the introduction of new electrochemical sensing devices, based on a wide range of chemical or biological recognition materials. In addition, mass production techniques (adapted from the microelectronic industry) enable the fabrication of extremely small and reproducible, and yet inexpensive (disposable), sensing devices. Such devices are being coupled with light and user-friendly microprocessor-based instrumentation.

Fast-responding electrochemical sensors are also being adapted for detection in on-line monitoring or flow-injection systems (as needed for continuous monitoring or field screening applications). Other advances of selective and stable recognition elements, “smart” sensors and molecular devices, remote electrodes, multiparameter sensor arrays or micromachining and nanotechnology, are certain to have a major impact on pollution control. Additional efforts should be given to the development of new immobilization procedures (that increase the stability of the biocomponent), to the design of new electrocatalysts (that facilitate the detection of additional priority pollutants), to the replacement of classical mercury electrodes with well-defined solid surfaces, to address the fouling and degradation of electrochemical sensors during use, to the development of immunoassay-based electrochemical sensors and of remote electrodes for unattended operations, and introduction of multi-sensor systems for simultaneous monitoring of several priority contaminants. On-going commercialization efforts, coupled with regulatory acceptance, should lead to the translation of these and future research efforts into large scale environmental applications.

Table 4-4.
Examples of Electrochemical Sensors and Biosensors for Environmental Analysis

Analyte	Recognition	Recognition Process	Transduction Element	Ref. mode
Benzene	Modulated microbial activity activity	Whole cell	Amperometry	28
Cyanide	Enzyme inhibition	Tyrosinase	Amperometry	25
Hydrazines	Electrocatalysis	Ruthenium catalyst	Amperometry	39
Lead	Ion recognition	Macrocyclic ionophore	Potentiometry	82
Mercury	Preconcentration	Crown ether	Voltammetry	47
Nickel	Preconcentration	Dimethylglyoxine	Voltammetry	46
Nitrite	Preconcentration	Aliquat 336 ion exchanger	Voltammetry	49
Nitrosamines	Electrocatalysis	Ruthenium catalyst	Amperometry	40
Peroxides	Biocatalysis	Peroxidase	Amperometry	16,17
Pesticides	Enzyme inhibition	Acetylcholinesterasecholine oxidase	Amperometry	16,17
Phenol	Biocatalysis	Tyrosinase	Amperometry	9-15
Sulfite	Biocatalysis	Sulfite oxidase	Amperometry	19
Uranium	Preconcentration	Nafion	Voltammetry	51

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Workgroup Discussion (by Joseph Stetter)

General Comments. Some of us on the panel were technology suppliers and other were technology developers, researchers, and scientist. We did our best to represent the needs of the users as well as the technical capabilities and possibilities of electrochemistry. As with any survey, it is best to take a broad view of the field and so we included electrochemical sensors of all types and even electrochemical techniques. Each of these areas of electrochemistry can contribute to the analysis of one or more organic, inorganic or Ionic species of interest in air, water or soil. Sensors and sensor systems were considered and these can be of potentiometric, amperometric or conductimetric variety (which includes what many consider solid-state sensors and even IMS).

There were several applications within most needs that would require different specifications. For example, a simple instrument to map the soil contamination by sniffing above the soil, a cleanup indicator to see if remediation is progressing, an on-site monitor to check the movement of the contaminant in the soil, the complete analysis and speciation of each contaminant of interest in the various soil matrices are only a few of the specific tasks that are possible. We recommend that the need (e.g. organic in soils) be identified by application (the field use of the data) as well as by chemical analysis (the specific compound(s) and analytical specifications (speciation, accuracy,...)) required. This will provide the definition needed to actually address the technology that is most suitable for the analysis . In general electrochemical methods tend to be low cost, low power (portable), disposable, and yet offer some accuracy, precision, sensitivity, and selectivity. Often the trade between a laboratory and field method is increased cost for assurance of selectivity and accuracy for the analytical result. But not every analysis required the ultimate selectivity and assurance and in fact screening tolls are cost-effective in many industrial applications for human health, safety, and environmental concerns. We feel these screening tools will come to be invaluable in DOE applications as well.

The five discussion areas or topics are covered for each need that was identified. The electrochemistry was discussed in its broadest terms and includes analytical methods (voltammetry, potentiometry, combinations with chromatography, etc.) as well as chemical sensors (potentiometric, amperometric, conductimetric). The needs were discussed from the points of view of the technical requirement, examples of technical products, the cost, the stage of requirement, examples of technical products, the cost, the stage of development and probability of success, and other general comments about the appropriate applications of electrochemistry to these problems. In general, electrochemistry will be appropriate for some of the applications and provide very cost-effective analytical tools.

NEED 1a, 2a. Organics in soil.

A. State of Practice, e.g. baseline technology used, if any.

There were no specific examples of completely commercial electrochemical sensor technology or devices that the US DOE was using at the present time for organics in soils. The closest examples we can produce are prototype devices for chlorinated hydrocarbon emissions above soils at Hanford and some downhole tests for hydrocarbons using amperometric sensors in a SCAPS probe.

The use of electrochemistry in DOE applications is most certainly in its infancy and will hopefully be the target of DOE investment so it can grow over the next few years.

B. Typical Technical Requirements of the need.

The basic problem here is the measurement of BTX, solvents, and special compounds of interest such as PCBs, Phenol, DNAPL, and TNT in may different soil environments. The sensor would need to be responsive at low PPM levels. Not all field jobs require all chemicals and so there will be applications for subsets of these compounds as well as analysis that are screening (fast and cheap) and laboratory (speciate, accurate,...)types.

There were several applications within most needs that would require different specifications. For example, a simple instrument to map the soil contamination by sniffing above the soil, a cleanup indicator to see if remediation is progressing, an on-site monitor to check the movement of the contaminant in the soil, the complete analysis and speciation of each contaminant of interest in the various soil matrices are only a few of the specific tasks that are possible. We recommend that the need (e.g. organic in soils) be identified by application (the field use of the data) as well as by chemical analysis (the specific compound(s) and analytical specifications (speciation, accuracy, ...) required. This will provide the definition needed to actually address the technology that is most suitable.

C. Current Capabilities of Emerging Technologies.
D. Short term capabilities.
E. Projected benefits.

There are several existing electrochemical sensors and sensor techniques that could be used for existing applications like characterization and workplace safety. These could also be applied as effective screening tools.

Electrochemical methods coupled with HPLC are of interest.

With adaptive samplers, many methods and sensors scan yield data of comparable quality to sample returned to powerful analytical labs. In addition, field techniques are made possible by electrochemical sensor s and instruments because they are typically simple and low power. This enables quality data, cost savings, and time savings to be often achieved together. Or, if the job requires low quality data (e.g., screening), the sampling can be simpler and faster; often useful trade-offs.

Concluding Remarks

1. Some commercially available sensors can be applied to DOE needs immediately.

There are commercially available electrochemical sensors that can be immediately applied to DOE needs and some are already in place but none appear to be as widely used as they could be. This can be due to a lack of knowledge of the sensors or a lack of uniform operating procedures within DOE. DOE needs both efforts at uniform procedures to efficiently operate or efficiently deploy any technology. Specifically, amperometric sensor for toxic gases and selective ion electrodes are commercially available and can be applied to DOE problems.

2. Some developed electroanalytical methods can be applied to DOE problems.

Sometimes electrochemistry can be used such as ASV for Pb or combined with liquid chromatography to create useful technology. Again, a lack of problem definition (in terms of multiple sites using the same solution) is often a problem.

3. Electrochemical methods and sensors can be developed to perform a unique need for DOE.

Electrochemistry is often a very low power, portable, and low cost alternative to many instrumentally intensive analytical methods. In this regard, where cost, portability and/or disposable sensors are useful, electrochemistry can often be the methods of choice and sensors can be developed for specific analytes and problems from gases (hydrogen, ammonia, chlorinated organics, CO,...) to liquid contaminants (Pb, Uranium,...)

4. Analytical systems enhance the ability of electrochemical sensors to solve problems.

Electrochemistry can be an approach for organic, inorganic and ionic analytes. Methods include potentiometric, amperometric, conductimetric type sensors. A sensors system can improve the selectivity and overall performance of a small electrochemical sensor. Research to improve and expand the use of electrochemical sensors, especially for organics and in micro-analytical systems, can make significant contributions to DOE problems.

<u>Recommendations</u>:

- DOE needs a better definition of its sites and their needs.
- DOE needs more uniform operating procedures to solve specific problems and apply technology when it is created.
- DOE needs to adapt current technology to solve a problem and then apply it to many sites to gain the efficiency that technology development is supposed to bring.
- DOE needs to develop new technology for problems that do not have solutions. Currently, uranium can be analyzed by ASV, and field equipment could be developed.
- DOE should do research on new technologies such as an electrochemical sensor for organics or u-eletrochemical instrument systems because these systems will have unique capabilities to deliver advanced analytical systems when they are needed.
- In short:
    - Do some Research;
    - Do some Development;
    - Do some Commercialization.

Research on electrochemical cells for organics, u-instrument systems that use electrochemistry are important. Development of sensors and methods that are needed for special applications or that need special adaptations to fill a DOE need such as ASV for uranium or the selective sensor for chlorinated organics or other such idea should be high priority. Commercialize or help commercialize ISEs, amperometric cells in applications where they are now needed such as workplace safety, characterization, process monitoring. The commercialization will be facilitated more by DOE internal communication of standard practices and development of methods to solve field problems and fill field needs.

<u>Field Deployable Instrumentation</u> by Richard Ediger, The Perkin Elmer Corp.

I. Description of the Technology

For the purposes of this discussion, fieldable instrumentation is limited to portable and transportable systems whose primary measurement system involves either separation or X-ray fluorescence technology. It specifically excludes laboratory instruments operated in a mobile field laboratory, products based on integrated sensors, and those using optical spectroscopic detection systems.

II. Needs Analysis

Of the many potential needs posed at the onset of the discussion, the following five analyte classes and matrices were deemed to be the most important for analysis using fieldable instrumentation:

- organic components in water
- organic components in soil
- organic components in air
- RCRA metals in water
- RCRA metals in soil

The discussion is complicated by the generality of several of the identified analyte classes and matrices. The term “organic components” for example includes species ranging from gasoline at high concentrations in heavily contaminated soil to trace dioxins in incinerator stacks. The term “water” may refer to relatively pristine drinking water to the supernatant from underground nuclear waste storage tanks. A discussion of the relevance to specific technology to specific needs therefore will of necessity be cursory and will cover only general principles.

<u>Baseline technology</u>

The current state of successful practice covers the broad scope of the general needs in a fairly complete manner. Table 4-5 identifies the primary technologies available from the two broad analyte classes.

These technologies are almost universally comprised of laboratory instrumentation scaled down in size to meet portability requirements. The performance of the fieldable systems often approaches that of laboratory methods for many samples. Sample handling procedures, too, are largely those currently employed in the laboratory.

Table 4-5
Technologies Available

Analyte Class	Current Technology
Organics	GC
	GC/MS
	MS
	supercritical fluid chromatography
	capillary electrophoresis
	HPLC
	ion chromatography
	photoionization, flame ionization,
	and electron capture detectors
	ion mobility spectrometry
RCRA Metals	X-ray fluorescence

Typical technical requirements

The technical requirements for fieldable instrumentation of the type this discussion addresses can be separated into those related to the physical nature of the instrumentation and those related to analytical performance. Since the definition we have chosen for "fieldable" is related to portability, the primary physical requirements are size, power, ruggedness, and use of consumables such as gases. Although a rigorous definition of portability could be stated, for the purpose of this discussion it can simply mean an instrument that is designed to be used outside of a laboratory and can be powered by batteries or a small generator.

Performance requirements for fieldable instruments are generally accepted to be less stringent than for laboratory equipment in terms of lower limits of detection, but the degree of accuracy for specific analyte species is often expected to be similar to that of laboratory analyses. Exceptions are for systems that are designed for screening of broad classes for compounds, such as the hand-held photoionization and flame ionization detectors for generic volatile organic compounds.

Projected short term capabilities of emerging technology

Emerging technologies for fieldable instruments are anticipated to continue to follow the previous trend of scaling down current laboratory instrumentation. For the near term this will be a continuance of utilizing current separation and detection concepts in ever smaller packages. On the horizon however is the transformation of these technologies from the macro to the micro world. The "GC on a chip" in a hand-held package has an opportunity for both acceptable performance and for market acceptance. Likewise, similar concepts for liquid phase separations are nearing commercialization. A bit farther into the future, but still foreseeable, is the miniaturization of mass spectrometry to bring systems such as GC/MS from their current "transportable" status to truly hand-held packages. The trends in portable X-ray fluorescence are likely to be in detector design, with both increased resolution and enhanced sensitivity. In short, the future for fieldable instrumentation appears to be relatively encouraging. Projected needs for the separation and detection technologies are on their way to being met.

However a related area that can be identified as requiring more emphasis is that of sample preparation. The host of separation methods share a variety of sample preparation and pre-concentration techniques such as purge and trap, solid phase extraction, thermal desorption, cryofocusing, membrane separation, microwave decomposition, and supercritical fluid extraction. The current trend for the miniaturization of the separation/detection technologies does not seem to be as successful for the sample preparation methods often required for the analysis of complex environmental samples. Recent innovations in laboratory-based sample preparation methods are making the transition to fieldable versions in a slower pace than might be desired. An exception to this general statement is the area of solid phase extraction. Methodologies that formerly required long columns of pre-concentration media are now successfully reduced to small packages that are compatible with portable instrumentation.

Projected benefits of emerging technology

The convenience benefits of the continued reduction in the size of fieldable instruments are readily apparent. A benefit of reducing the size of separation techniques that should not be overlooked is that of analysis time. Separations that may take 30 minutes in a laboratory instrument may proceed in a few minutes when the path length and cross-sectional area of the separation device is reduced by a factor of ten. This time savings translates to more samples per day and allows a given physical sampling site to be characterized more completely at less cost.

A real leap will be achieved when the performance of these field systems more closely approaches that of a laboratory-based instrumentation. At that point, a field analysis will no longer be seen to be the poor brother of laboratory work and the trend to move the lab to the field will be greatly accelerated. The reduction of the size and complexity of the sample preparation methods will play a major part in this shift and deserves increased attention.

Immunosensors by Edward J. Poziomek, Old Dominion University

I. Description of the Technology

For the purpose of this discussion, the term immunosensors encompasses immunoassay kits and biosensors (Figure 4-6). Immunoassay kits represent a mature technology while biosensor technology is emerging. Biosensors are defined as analytical devices composed of biological sensing elements in contact with physical transducers which together relate concentration of analytes to a signal[12].

Attractive attributes of immunoassay kit and biosensor technologies include a combination of sensitivity (ppb-ppm) and high selectivity, and flexibility in format. The use of immunoassay kits in the field is beginning to be accepted by the regulatory community (Figure 4-7).

IMMUNOASSAY TECHNOLOGIES APPLIED TO THE FIELD

- MATURE
  IMMUNOASSAY KITS
- EMERGING
  BIOSENSORS

(ANALYTICAL DEVICES COMPOSED OF BIOLOGICAL SENSING ELEMENTS IN CONTACT WITH PHYSICAL TRANSDUCERS WHICH TOGETHER RELATE CONCENTRATIONS OF ANALYTES TO A SIGNAL)

Figure 4-6

IMMUNOASSAY KIT AND BIOSENSOR TECHNOLOGIES

ATTRACTIVE ATTRIBUTES

- COMBINATION OF SENSITIVITY (ppb-ppm) AND HIGH SELECTIVITY
- FLEXIBILITY IN FORMAT
- BEGINNING TO BE ACCEPTED BY THE REGULATORY COMMUNITY

II. Needs to which the technology applies

Figure 5-7

[12] Kim R. Rogers and Edward J. Poziomek, "Environmental Applications of Biosensors: Opportunities and Future Directions," Proceedings of the 1993 U.S. Environmental Protection Agency and the Air and Waste Management Association, Field Screening Methods for Hazardous Wastes and Toxic Chemicals, Volume 1, Las Vegas, NV, February 1993, pp. 26-33.

Figure 4-8 lists priority needs which can be met now using existing technology. Organic analytes in water and soil are already being detected using commercially available immunoassay kits. In situ detection is more complicated and at the present time requires the sample to be brought to an operator with an immunoassay kit. Automated detection/monitoring such as with a biosensor will require further technology advancements and field experience.

PRIORITY NEEDS WHICH CAN BE MET WITH
IMMUNOASSAY KIT AND BIOSENSOR TECHNOLOGIES

NEED	APPLICATION
MONITORING ORGANICS IN H_2O	PROCESS MONITORS
DETECTING (ANALYSIS) INDIVIDUAL ORGANICS IN H_2O/LIQUIDS	EFFLUENTS MONITORING
DETECTING INDIVIDUAL ORGANICS IN SOIL	SUBSURFACE CHARACTERIZATION AND CONTAINMENT MONITORING
DETECTING INDIVIDUAL ORGANICS	
SOIL IN SITU H_2O IN SITU	SUBSURFACE CHARACTERIZATION AND CONTAINMENT MONITORING

Figure 4-8

Figure 4-9 lists priority needs which may be met with immunoassay kit and biosensor technologies but additional work is needed to develop the necessary biological materials before applications can be pursued. Development of, for example, antibodies for RCRA metals, radioactive metals and various inorganic compounds, presents significant technical challenges.

PRIORITY NEEDS WHICH MAY BE MET WITH
IMMUNOASSAY KIT AND BIOSENSOR TECHNOLOGIES

- DETECTING INDIVIDUAL ORGANICS IN AIR
- DETECTING RCRA METALS IN WATER AND SOLIDS
- DETECTING RADIOACTIVE METALS IN WATER, SLUDGE AND SOLIDS
- DETECTING INORGANICS IN WATER

Figure 4-9

Detecting individual organics in air presents challenges in format development and requires work on appropriate sampling procedures. Immunoassay kit and biosensor technologies could benefit from more attention to sampling and sample handling in general.

Baseline technology. As mentioned above, commercially available immunoassay kits represent a mature technology. There are a variety of available formats for a number of organic pollutants depending on the need. There are a number of reports on the use of immunoassay kits in the field. The U.S. Environmental Protection Agency Field Screening Symposium held biennially in Las Vegas (next one in 1997) has brought together many practitioners who describe their experiences. Use of immunoassay kits in the field, e.g., during remediation, has saved considerable resources in analytical costs and field labor/equipment costs

Typical technical requirements. Technical requirements include a combination of sensitivity (ppb-ppm) and high selectivity in field screening and field monitoring. Immunoassay kits are being used for field screening. Single use biosensors are also available. Development of continuous and in situ monitoring remains a high priority but advancements are needed in biosensor development.

Current capabilities of emerging technology. Some of the major technology challenges in improvement of immunoassay kits and biosensors are given in Figure 4-10. Biosensor technology is emerging. Single use biosensors (e.g., immunoassay kits with electrochemical detection, test strips and dipsticks) are available. However, important issues such as data quality objectives, reversibility, sample preparation requirements, dilution and matrix effects, and requirements for addition of tracers, cofactors, etc., need to be considered when designing biosensors for monitoring applications.

MAJOR TECHNOLOGY CHALLENGES

IMPROVEMENT OF IMMUNOASSAY KITS AND BIOSENSORS

- BIOMATERIALS THAT CAN DETECT:

    ORGANIC VAPORS
    METALS
    RADIOACTIVE METALS
    VARIOUS INORGANICS

- INTEGRATION OF SAMPLING TECHNOLOGIES AND SAMPLING HANDLING METHODS TO MEET SPECIFIC NEEDS

Figure 4-10

Projected short-term capabilities of emerging technology. Major improvements to immunoassay kit and biosensor technologies in the short-term will depend on how fast technical barriers are overcome. Examples of technical needs include: new biomaterials for compounds of environmental concern; improved immobilization, stability and shelf-life of the biomaterials; biomaterials that can be used to detect organic vapors and metals; and integration of sampling technologies with specific biosensors to meet specific needs.

Projected benefits of emerging technology. The major benefit seems to be projected cost savings of 50% on the average relative of laboratory methods (Figure 4-11). The probability of technical development success is estimated to be 30-50% over the next ten years. The investment and time required to bring products to market is estimated to be two to four years from proof-of-concept at a cost of $1-4 million per product. This may be conservative in cases for which field experience is limited. In situ monitoring systems are examples.

ESTIMATES RELATIVE TO USE OF AND
IMPROVEMENTS IN IMMUNOASSAY KIT AND
BIOSENSOR TECHNOLOGIES

COST SAVINGS: 50% ON THE AVERAGE RELATIVE
TO LAB METHODS

PROBABILITY OF TECHNICAL DEVELOPMENT
SUCCESS: 30-50% OVER NEXT 10 YEARS

INVESTMENT AND TIME REQUIRED TO BRING
PRODUCTS TO MARKET:
2-4 YEARS FROM PROOF-OF-CONCEPT
$1-4 M/ PRODUCT

Figure 4-11

Field Deployable Instrumentation - Subsurface by Mitchell Erickson, Argonne National Laboratory

Sensors and instruments in this category can detect, identify, and quantitate individual organic compounds or classes of compounds in soil in-situ. This category of sensors/instruments does not include those which could detect “carbon” nor laboratory-based instrumentation. There is a considerable gray area between the “lab” and true *in*-situ instruments or field-portable instruments for which samples must still be obtained and transported (even if only over a short distance).

This workgroup concentrated on two high priority needs relevant to the use of subsurface instrumentation:

organics in soils
individual inorganics and RCRA metals in soil

Before identifying field deployable subsurface technologies applicable to these needs, the workgroup assessed the technical specifications required to meet a need for five types of applications:

Characterization
Characterization for Screening
Monitoring During Remediation
Long-Term Monitoring
Closure

These specifications are included in Table 4-6. Specifications for Characterization are generally set to meet regulatory specifications. Following specification assessment, the relevance of specific technologies to the needs were rated, assuming deployment would be done using a cone penetrometer (CPT).

Table 4-6
Specifications for Subsurface Field Deployable Instrumentation

Specification Category	**Character-ization**	**Character-ization for Screening**	**Mon. During Remediation**	**Long-Term Mon.**	**Closure**
Qualitative	95% confidence	Not	Low	Low	90% confid.
Precision	SW-846	Not	Not		
Accuracy	SW-846	Somewhat	Somewhat		
Limit of Detect.	SW-846	Site-Specific	SW-846	SW-846	
Size	(CPT--<1” dia)	(CPT--<1” dia)			
Portable	Yes	YES!	moderate	No	
Power					
Cost	Cheaper than Lab	Cheap	Moderate	Cheap	Cheaper than Lab
User Friendly	so-so	YES!	so-so		
Data Availability	near-real time	Real time	Not the rate-limiting step!	No con-straints	Slow=OK

Technology Specifications for "Individual Organics in Soil in Situ."

Given the specifications in Table 4-6, the technologies listed in the Table 4-7 were rated by probability of success in bringing a product to market within two years for the characterization and/or monitoring of organics in soil. Estimates on cost to market and potential cost savings associated with these technologies could not be made.

Table 4-7
Technologies for Subsurface Field Deployable Instrumentation Applied to the Assay of Organic Compounds in Soil

Technology	Cost	Success Probability	Comments
Surface Acoustic Wave Devices	$5K Cap	90%	
Purge & Trap /Fast Gas Chromatography		70%	
Laser Induced Fluorescence		99%	at market
Fiber Optic Chemical Sensors		99%	near market
Photo Ionization Detector		90%	reasonable for use with CPY
Flame Ionization Detector		60%	
Immunoassay		70%	
Capillary Electrophoresis		25%	In lab, done on microscope slide scale
Gas Chromatograph in CPT		10%	
UV/VIS Spectroscopy			Doable, but utility is questionable
Raman Spectroscopy		20%	

On-site lab = 60% cost savings
CPT saves 25% vs. drilling

Technology Specifications for Individual Inorganics & RCRA Metals in Water"

Sensors and instruments in this category can detect, identify, and quantitate individual metals and inorganic compounds or ions in aqueous media.

In general, the objective must be to detect and quantitate individual metal ions, i.e. a "total inorganic analyzer" would be swamped by common, but generally not target, ions such as sodium, calcium, and magnesium. For most analytes of interest, low detection limits, high selectivity, and high specificity are required. The optical emission/absorption spectra, X-ray spectra, mass spectra, and electrochemical techniques are most often used for metal ion analysis. With appropriate chromophoric chelating agents, optical absorption, fluorsescence, and other related spectral techniques can be used.

Development in the area relies on incremental improvements on existing techniques such as better sample introduction, more sensitive detection, and enhancing field portability of laboratory instrumentation. Applicable existing techniques are included in Table 4-8.

Table 4-8
Technologies for Subsurface Field Deployable Instrumentation Applied to the Individual Inorganics & RCRA Metals in Water

	Cost	Cost Svgs/10 y	Success prob.	Cost to Mkt.	Ranking
LIBS		50			
N Bombard.		90			
XRF		50			

It was the general conclusion of the working group that innovative in-situ and portable sensors/instrumental technologies can save 60-80% of Site Investigation Costs through:

- Lower per-sample costs
- RE-mobilization
- Reduced needs to re-write reports (a cost of $20,000 was quoted by a participant)
- Reg. Agency Report Review Charge (a state cost of $5-25,000 per report was quoted by a participant.)
- Reduced Waste generation
- Ability to better target the remediation
- Lower overhead (less time)

<u>FORUM ON CHEMICAL SENSORS AND FIELD DEPLOYABLE INSTRUMENTATION</u>.

The Forum was held on the day following the completion of the workshop as part of the Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy. Summaries of the market study results and the evaluation of needs by commercial potential were presented. Discussion leaders from the Workshop technology workgroups served as an expert panel at the Forum

Members of the Forum audience were asked to present "case studies" of field assays where deficiencies in current methods were found to exist. Several "case studies" were presented and discussed with expert panelists, audience members, and Forum moderators making comments.

Audience comments included the following input

- Regulator involvement in new technology development and acceptance of new technologies is very important.
- While some large companies are working for the acceptance of field methods, smaller companies cannot afford the cost of obtaining regulator acceptance.
- The analysis of Hanford tank headspace gases and tank wastes is a very significant DOE problem.
- Data quality objectives (DQOs) must be considered as part of technology development.
- Sampling and documentation of sample locations are important issues in designing field deployable analytical methods.
- DOE needs sensors for Sr^{90}, Cs^{137}, and Cr^{VI}.
- DOE should focus on most urgent problems such as situations where contaminants are in contact with ground water.

This Forum served as a platform to disseminate the information and conclusions summarized at the workshop to a wider base of interested parties while getting valuable feedback. The Forum lasted over 2 hrs and attracted a total audience of 128 people.

CHAPTER 5

RECOMMENDATIONS AND CONCLUSIONS

Strategy for Recommendations

The purpose of this work is to provide recommendations and to gain better insight into how to most effectively promote the development and implementation of new technologies to address DOE EM needs. Recommendations can be formulated in two important ways. Firstly, one can identify the emerging or adaptable technologies which have the highest potential to meet the needs. Improved insight and overview in this area is provided by the Workshop discussions on new technologies (Chapter 4) and by the database compilations of existing commercial products.

Given the identification of technologies having good potential to meet EM characterization and monitoring needs, recommendations can be derived by identifying situations where commercial development can be expected to play an important role in providing new technologies. Such situations will occur when DOE EM needs are similar to significant commercial needs and when DOE needs independently generate a substantial commercial demand for instrumentation. In such cases, a useful tactic would be for the DOE to encourage commercialization of needed technologies as soon as possible. Commercial demand would then drive product engineering and marketing efforts. The use of new commercial technologies at DOE sites could be encouraged through programs designed to demonstrate and validate the performance of the new products.

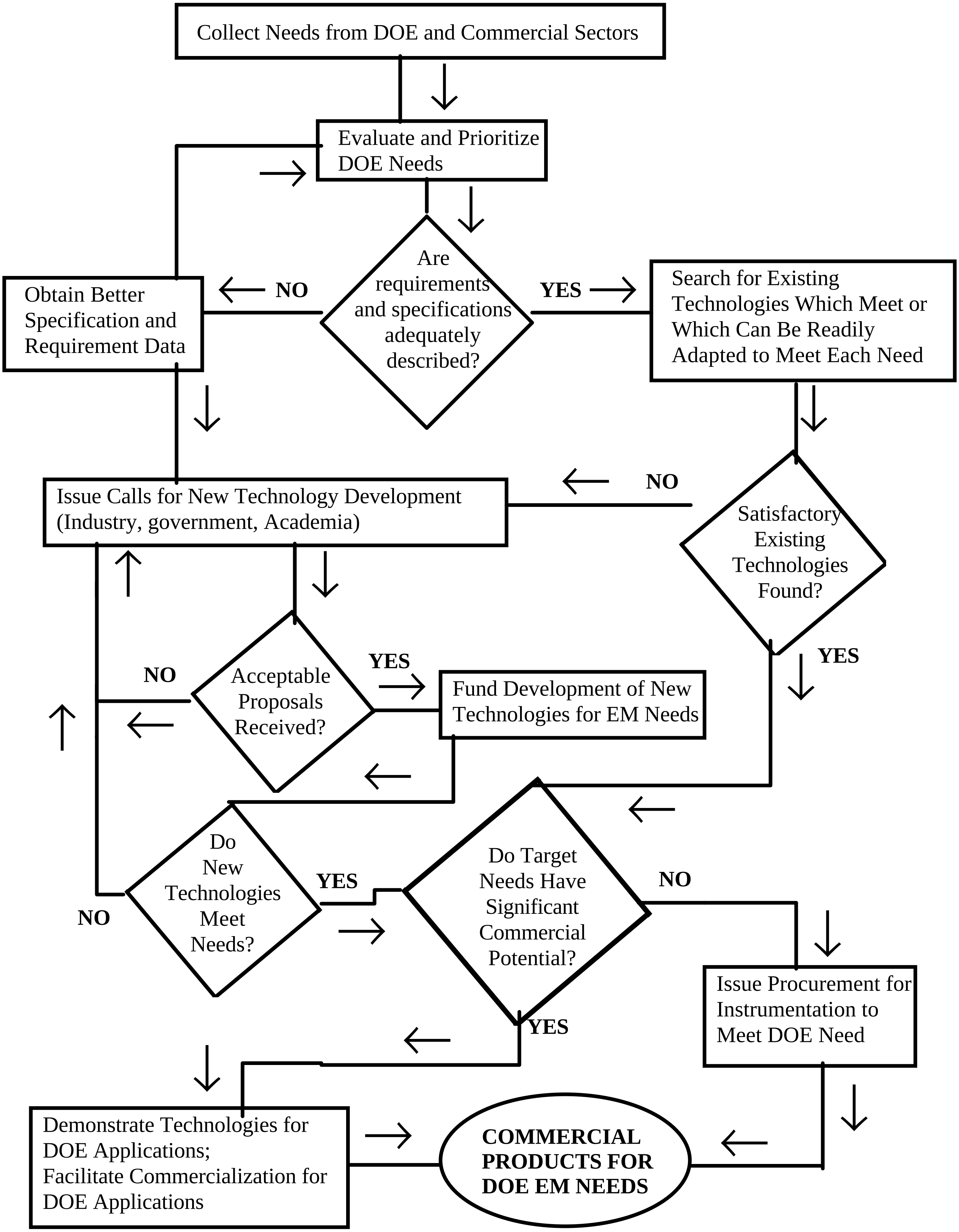
The market evaluations and the market study described in this report were designed to estimate the magnitude of commercial potential and to estimate how that potential might be distributed over general classes of needs. The needs rankings and the Workshop needs discussions aid in the identification of overlaps between DOE needs and commercial needs which could lead to enhanced commercial development. Results from these studies now can be used to formulate general strategy for technology development.

Recommended Strategies for Technology Development.

A recommended strategy for technology development is contained in the flowchart shown in Figure 5-1. As indicated in this figure, the first step in the process must be the collection of needs. Regardless of potential commercial demand, the effective development of technologies to meet any stated need requires a critical evaluation of the need which results in clear, quantitative performance and cost specifications. Neither DOE nor commercial developers can design an effective characterization or monitoring system if well founded requirements and specifications are not known or available. Feedback from commercial developers at the Workshop included comments that many DOE needs were not described in sufficient detail for them to determine what was required to meet the need.

Given adequate needs descriptions, a thorough search of methods or technologies which are known to be capable of meeting the stated need or similar needs must be done. The results of such a search can be used to establish a technology baseline which can serve to identify existing performance specifications and which can serve as a comparative reference to evaluate the

Figure 5-1 STRATEGY FLOWCHART FOR TECHNOLOGY DEVELOPMENT



potential improvement offered by proposed new technologies. Baseline technologies can also serve as candidates for adaptation to desired performance specifications.

If it can be documented that baseline technologies are nonexistent or cannot meet performance requirements, calls for the development of improved technologies must include all needs specifications and baseline technology information gathered to justify the call. Calls for new technology development to meet needs having significant commercial potential may best be directed to commercial developers. New technologies for more DOE specific needs with low market potential may be best done through collaborations of DOE laboratories, universities and commercial firms. DOE laboratories must be involved when access to DOE sites or materials is important for success.

Marketing of New Technologies.

Once development of new technologies is in progress, plans must be made to market the intended final product to the end users, DOE field personnel and commercial customers. Sensors and field deployable instrumentation must be developed to the point that end users will be able to realize significant advantages over baseline technologies. Several aspects of this marketing process must be considered:

- Technical advantages must be clearly delineated to all potential users
- Cost advantages must be determined and presented in a realistic manner
- The equipment required to implement a new technology must be readily available via ownership or service contractor
- Training on the implementation of new technologies must be readily available
- Maintenance, service, and replacement parts must be readily available.

These recommendations imply that new technologies must have the attributes of competitive commercial products. If significant market demand exists for specific new technologies, then commercial developers seeking to capture market share will perform all needed marketing functions. However, if significant market potential does not exist, then the marketing of new technologies to DOE end users becomes the responsibility of the DOE technology development (TD) program. There are several activities which can be pursued by DOE TD (EM50) in collaboration with DOE personnel responsible for waste management (EM30), for environmental restoration (EM40), and for facility transition and management (EM60) to provide the marketing needed for product acceptance and use within the DOE.

Field demonstrations are one means being used to establish the technical and cost performance specifications of new technologies and to inform end users of their capabilities and availability. However, user acceptance and the credibility of demonstration results are a critical issues. For field demonstrations to be effective marketing tools, they must be done in a well controlled and objective manner. Evaluation of results should be done by an independent third party, and the accuracy of data must be judged via the use of confirmatory testing methods. Evaluations of demonstrations and their significance should be made public and brought to the attention of all potential users. Programs to provide this type of technology demonstration already exist and include the Consortium for Site Characterization (a collaboration of the DOE, DOD, and EPA) and the Rapid Commercialization Initiative (RCI) (a collaboration of the DOE, DOD, Dept. of commerce, EPA, the Western Governors' Assoc., the Southern States Energy Board, and the State of California EPA). The services of these programs can facilitate the effective marketing of new technologies aimed at DOE needs. These programs are most effective for new technologies which have potential at many DOE site applications.

Another element of strategy which may be used to market new technologies within the DOE complex is to form teams of EM50 personnel with EM30 or EM40 workers and assign them the task of defining the technologies and procedures to be used to address specific DOE problem areas. A current example of such a collaboration is the Hanford Tank Initiative (HTI). In this effort, there is a team of EM30 and EM50 personnel who are identifying the procedures and technologies necessary to close underground storage tanks to the satisfaction of regulators, the DOE, and stakeholders. Similar collaborations are recommended for the full range of DOE problems.

Both strategies for development and implementation require use of instrumentation which has been developed to at least field prototype stage and preferably to commercial prototype status. Technologies should become available for sale with technical support to end users as soon as specifications are met and preliminary user acceptance is achieved. This requirement argues for commercial firms to undertake virtually all manufacture and support of instrumentation based on new technologies because they have the most experience. Thus, technology transfer of technologies developed under DOE funding at non-commercial sites to commercial developers is a critical step in placing new, improved technologies into routine field use. In cases where significant commercial potential exists, licensing of technologies and subsequent technology transfer should be a straightforward process because potential commercial partners will be motivated to acquire the new technology by potential sales and profit.

For technologies aimed a meeting specialized needs with little overall market potential, commercial partners can best be attracted to licensing and transfer arrangements by establishing a market within the DOE that promises some minimum level of sales at prices which allow a reasonable return on investment. It is recommended that as new or existing technologies to meet DOE needs are developed to the point where they can meet performance specifications, then procurements should be issued which will cover both field testing of offered technologies and the purchase of best performing instrumentation. Such procurement efforts should be a partnership between EM50 and EM30 or EM40 personnel. This approach is similar to that employed by the DOD to acquire sophisticated military hardware which does not have a commercial market.

Conclusions.

- DOE EM needs relevant to characterization, monitoring and sensors technologies can be differentiated into two groups: those that have commercial market potential and those that do not.
- It is important that performance specifications for all needs be specified in as much detail as possible. Descriptions can be extended beyond what currently exists for many needs.
- Available and adaptable technologies which can potentially meet a need should be seriously considered before any calls for new technology development are issued.
- Calls for new technology development can be directed to industry and/or DOE laboratories and universities on the basis of the commercial potential of the need:

    - TD for needs with significant commercial potential can be directed to industry.

- All new technologies must be marketed to the end users, and EM50 can take a leading role in such marketing efforts.
- Virtually all instrumentation manufacture and technical support can be done by commercial entities.

CHAPTER 6

PERFORMANCE ASSESSMENT AND LESSONS LEARNED

Critique

All workshop participants were formally encouraged to critique the market study and Workshop efforts. In addition, the Unimar group did a self critique of their market study. From these comments and from oral feedback from interested parties a number of "lessons learned" were identified.

Workshop Evaluation. To aid determination of the effectiveness of the Workshop, survey forms were given to participants to obtain comment and feedback. The following seven questions were asked in the survey:

- What is your assessment of the Workshop? (rank excellent, very good, good, poor)
- What did you expect to gain from attending the workshop?
- Did the Workshop meet your expectations? (yes, partially, or no)
- What did you like/dislike about the Workshop?
- Did the workshop accomplish its objectives of identifying technology needs for development and prioritizing technology development in accordance with market potential?
- What would you change about future workshops of this kind?
- Other comments?

The assessment ratings obtained were as follows:

Excellent	2	Fair	9
Very Good	4	Poor	2
Good	11	No Rating	1

The most common expectations were:

- obtaining a better understanding of DOE interests and industry involvement with DOE
- obtaining an interaction between vendors and users and learning more about user requirements
- obtaining a better understanding of the needs for chemical sensors in the market place

Participants felt expectations were met as follows:

Yes	4	Partially	21	No	5

The reasons that many participants felt their expectations were not completely met were commonly:

- There was an insufficient number of end users participating in the Workshop.
- Instrument developers did not share proprietary marketing information.

Other likes and dislikes about the Workshop included:

- There were good technical discussions and opportunities to “network” with individuals in the sensor community.
- There was a good cross-section of the government and private sectors.
- The market study needed more time and research; the results were not highly informative.
- The market study was too limited in scope.
- There was too much emphasis placed upon assigning dollar values to market potential.

Participants felt objectives were met as follows:

Yes	3	Partially	16	No	10

Changes recommended for future workshops included:

- Increase representation from end users (as much as 50% from one comment).
- Focus on general trends and concepts.
- Do not try to get more detail than is feasible.
- Obtain more participation from DOE focus areas.
- Separate discussions by market parameters, not technical parameters.
- Provide more scheduling information and workshop materials to participants in advance of the meeting.
- Provide more information to the participants.

Other comments included:

- Beneficial contacts were made.
- The workshop was useful.
- Good format but wrong participants.
- The market study should have been done more broadly.
- It was clever to connect the Workshop with Pittcon.
- Quantification of the market is a difficult but useful endeavor.

Unimar Critique of Market Study.

by The UNIMAR Group, Ltd., May 15, 1996

We would like to preface this critique by stating that overall we felt the project was a success. The study achieved its stated goals of determining what instrumentation is currently being used, what applications are most common, what new capabilities are most valuable to users, and what commercial markets are most attractive. In addition, vendors were identified, current instrument sales and future market potentials were determined, and a set of market needs was classified and organized. However, we recognize that the findings could have had a higher level of certainty and provided value for a wider constituency. We have identified three circumstances which we feel have most limited the findings of the project:

- Budget limitations;
- Schedule complications;
- Scope definition.

Budget Limitations

As in any project, the results are limited by the available resources. In the case of the market study, a larger budget would have allowed for further sampling of both equipment users and equipment vendors, supplying a data set with a higher level of confidence.

Schedule Complications

The project was originally proposed to commence on November 20, 1995, with a compressed twelve week project duration. Due to conditions beyond the control of both parties, the actual project commencement was delayed to December 18, 1995. This delay forced an accelerated project schedule to complete certain deliverables by a target date of February 26, and the resulting project schedule was extended to 13 weeks. This compressed time frame also limited the number of interviews which could be conducted, which in turn limited the results. A majority of the deliverables were delivered on schedule during the week of February 26, 1996 prior to the Workshop. It was agreed by both parties to extend the final delivery from March to May in order to ensure proper review of the final project report. We feel that more preparation time prior to February 26 would have contributed to more robust findings.

Scope Definition

The definition of the scope of the project was a topic which arose early in the project as the survey instrument was being developed. As the project progressed, it became clear that the original scope of the project would limit the value of the results in some readers' opinions. Research in the narrow market for environmental field instrumentation led to overlapping markets for chemical sensors, such as industrial process monitoring.

A broader project scope would have increased the value of the results, and increased the number of technology developers and equipment users for which the results have value. Unfortunately, broadening the scope of the current project to include all of these other markets was unrealistic given the time and cost constraints. Even if the original project scope included these other areas, requirements for additional interviews and additional secondary research would have required expansion of the original budget and schedule. With the number of interviews conducted constant, a broader project scope would have resulted in less accurate results.

The scope of the project was the one item outside of the obvious budget and time constraints which we feel limited the usefulness of the results. For practicality, however, defining the scope of the project to only include environmental field instruments for site characterization, waste characterization, and environmental remediation process monitoring in the U. S. ensured that the project could be completed within the given parameters and still yield useful data and findings.

Lessons Learned

Valuable lessons were gained from both the execution of the market study and the Workshop. The success of both endeavors were heavily influenced by the scope and details of the lists of needs provided from the DOE EM focus areas. The providers of the market study, Unimar, used the needs lists to define the scope of their study to determine commercial demand for sensors and field deployable instrumentation from all sectors of the economy. A combined list of needs also played a prominent role in workshop discussions because market potential and the importance of emerging technologies were both assessed using the needs list as a reference. Difficulties in obtaining accurate estimates of market potential and specific technology recommendations arose, in part, because many needs were not specified in sufficient detail. Thus the first major lesson learned was

- **DOE EM needs for improved technologies must be specified in as great as detail as possible.**

During discussions at the Workshop, it became apparent that descriptions of needs were required in greater detail, but few participants could provide such information because the end users of EM technology were under-represented despite efforts to invite such people. Thus, a second major lesson learned was that:

- **the ultimate customers, end users, of new technologies must be involved in both the needs definition process and the evaluations of new technologies for EM applications.**

Considerable effort was also made to assign quantitative values to the market potential of each of the many EM need categories in an effort to demonstrate attractive commercial opportunities. However, the scope of the market study was too limited to allow estimates of complete market potential, and the Workshop participants did not have or could not reveal sufficient information to make quantitative estimates. The "lesson learned" from this difficulty was that:

- **accurate and detailed quantitative marketing information for the sale of instrumentation for environmental characterization and monitoring is not publicly available, may not exist, and would require substantial resources to obtain.**

A major success of the Workshop was the attendance of a large number of commercial vendors of instrumentation. These vendors had an obvious interest in learning more about the market for instrumentation directed toward the environmental characterization and monitoring market. Many vendor comments, however, indicated that there is still considerable uncertainty with regard to what specific instruments and capabilities will be needed most. The lesson to be gained from these observations is that:

- **commercial vendors of instrumentation have a significant interest in the environmental market, but better market definition is needed before new product introductions can be expected**

Finally, in retrospect a good deal of information has either been developed or validated with regard to DOE needs, the overlap of needs between the DOE and commercial sectors, and the relative market potential of instrumentation capable of meeting DOE and commercial needs. This effort thus has been a beginning step towards obtaining the implementation of new technologies for environmental applications via the commercial supply pathway. Further development efforts in this arena should progressively lead to a series of successful technology implementations. The lesson from the finite but limited successes of this effort is:

- **the identification of needs, evaluation of market potential, and the encouragement of commercial instrumentation development for EM needs may be best addressed by a series of iterative efforts which can be successively applied until the desired level of success is achieved.**

APPENDIX A

Unimar Market Study

APPENDIX B

Discussions of Needs Workgroups

GROUP 1: SUBSURFACE CHARACTERIZATION
Reported by Mark Collins

Needs Ranking

Priority	Need
1	Detecting individual organics in water in-situ
2	Detecting individual organics in soil in-situ
3	Detecting individual organics in soil
4	Detecting DNAPLs in water in-situ
5	Detecting DNAPLs in soil in-situ
6	Detecting DNAPLs in water
7	Detecting DNAPLs in soil
8	Detecting individual RCRA metals in water in-situ
9	Detecting individual RCRA metals in soil in-situ
10	Detecting individual RCRA metals in soil
11	$Detecting inorganics and other contaminants in water in-situ
12	$Detecting inorganics and other contaminants in soil in-situ
13	$Detecting inorganics and other contaminants in soil
14	Detecting individual radioactive metals in water in-situ
15	Detecting individual radioactive metals in soil in-situ
16	Detecting individual radioactive metals in soil

Rationale for needs groups ranking order

Drivers -Federal and State Regulations are variable
- cost is key

Cost savings

Removing costs from the lab
Cutting sample collection, extraction, and preparation

In-Situ offers cost effective solution

Other Significant Needs

Physical Characteristics
Examples:

- Density
- Porosity
- Oxygen content
- Conductivity
- pH

Geomechanical

- Flow - subsurface plume migration
- Soil matrices - Cone Penetrometer
- Sample collection
- Sample extraction
- Sample preparation
  - Includes: Purge-and-trap
    - Cryofocussing
    - Auto-sampling (headspace)
- Data Collection and Management

Soil Gas Characterization - Organics

Bioremediation

Vadose Zone Characterization

DNAPLs

- No baseline subsurface characterization technologies
- All surface characterization

OVERALL BASELINE TECHNOLOGIES

Geiger counters
Neutron Activation
Alpha-Tracker

Portable GC - using for detection:

- PID
- FID
- ECD
- TCD
- AID
  - with purge-and-trap / thermal desorption

Portable GC/MS
Portable MS
Cone Penetrometer Sensors
IR - TPH
Immunoassay Kits
Fiber Optics - Petroleum contamination

HACH Kits - Sulfites, Nitrates, Phosphates, Amines
ICPs
Atomic Emission Spectroscopy
Raman Spectroscopic Techniques

CURRENT TECHNOLOGIES IN DEVELOPMENT

Fiber Optic Sensor Arrays
Metals
pH
VOC
Enhanced specificity through fluorescence polymer coatings
Immunoassay
Ion Mobility Spectrometry
FTIR

SOME KEY TECHNOLOGY PERFORMANCE CHARACTERISTICS

- Field rugged
- Easy to use
- Reliable
  1. Accurate
  2. Precise
- Wide Analytical Scope
- Screening
  1. Total VOC
  2. Total Petroleum Hydrocarbon (TPH)
- Characterization -
  1. Specificity
  2. Interference-free
- Sensitivity

  PPB
  PPM
  Parts-per-thousand

<u>Discussion Summary</u>

In-Situ Sensors

Three most significant needs are

1. Organics in situ soil (pervasive problem. major concern. amenable. toxicity.)
2. Organics in situ in water
3. Organics in soil.

Might be able to cut half of cost of lab analysis. (PCB example --- Erickson)
Must reduce number of false negatives.
In situ sensors need better performance, selectivity, and sensitivity.
Cost saving can come from:

- char.
- remediation

What are data gaps?
What are assumptions? etc.

Organic Vapor Monitoring is one baseline (screening) technique, but it is not really comparable to regulator decision level data.

GROUP 2: CONTAINMENT MONITORING
Reported by Lamar Jones

Technologies applicable to characterization and monitoring as a function of sample type and sample matrix (brackets, [ ], indicate commercial availability)

Sample Type →	radioactive metal	RCRA metal	Organics
Sample Matrix ↓			
water in situ	[stripping voltammetry] chem. flow probe		[immunoassay IA], Fiber optics, LIF, [GC/MS], SAW, [GC], SERS
soil (sample)	[B-Spec, α-Spec γ- Spec, XRF,] [ICP, AES/MS], LIF, [LIBS]	[Flame AA, XRF, LIBs, Strip volt, ICP, AES/MS]	[GC/MS, PID/FID, Fiber Optics, IA, GC]
soil in situ	surface: LIBs, XRF, ...-Spec Subsurface: LA, AES/MS		LIF, Raman, SAW, MOS, [Fiber Optics, Air sampled FTIR]
containers	Elec. Resistance Tomog. [Acoustic Res.] Ident by n-activation		[PID/FIDS, IMS,] [Catalytic Bead,] [MOS, GC, IR, Electrochemical]
sludge (sampled)	[ICP - MS/AES]		? Raman, [GC, GC/MS]
Sample Type →	DNAPLs	Inorganics	
Sample Matrix ↓			
water in situ	SERS, fiber optic	[FTIR, FIA, Sel. Ion Elec., Ion Chrom.]	
soil (sample)	x	see RCRA metals	
soil in situ	x		
containers	x	?	
sludge	x	see soils	

Comments

Requirements

specificity -> site specific -> 10
containers -> important -> 10
sensitivity 7
continuous vs. periodic (time) -> hourly + stability/durability -> 10
cost -> 0 -1 +2
in - situ ->10
false alarms -> less important 10
continuous (area/perimeter) vs. point detect.

networkable -> 10
reliability
sensor fusion -> 10

DOE needs: not specific enough to focus commercial product development

Discussion Summary

Needs statements are not specific enough.

Community developers not convinced that market is large enough to support development.

Landfill management is likely largest need.

Chemical sensors capabilities crosscut many application and industry areas.

Pollution presentation is one of those that crosscuts industries, i.e. is a DOE need that overlaps with industrial needs, thus representing a large commercial market.

Key crosscutting application is pollution prevention which requires chemical sensors

- for process monitoring
- for leak detection
- for mass balance monitoring
- liability minimization

Ranking seems parallel to subsurface characterization result

1. organics in water in situ
2. organics in soil in situ
3. organics in soil

Other Needs

Technology must have regulatory acceptance.

Baseline technologies for large Underground Storage Tanks:
out of tank monitoring wells
UST
magnetostrictive level monitors
vapor sensors

Desirability

Liability

Lateral technology transfer (LTT):
Need to detail needs specifically to drive LTT.

GROUP 3: SURFACE DECONTAMINATION FOR D&D APPLICATIONS

Reported by Eric Hess

Needs Ranking

Priority	Need
1	Detecting individual radioactive metals in metal, concrete, other solids
2	Detecting individual radioactive metals in asbestos
3	Detecting individual RCRA metals in metal, concrete, other solids
4	Detecting individual RCRA metals in asbestos
5	Detecting individual organics in metals, concrete and other solids
6	Detecting individual organics in asbestos

Needs Descriptions

need: detecting individual radioactive metals in concrete, other solids
current state: physical sampling, alpha, beta and gamma counters
key performance char.: speciation (energies), isotope information $U^{235, 238}$, below free release standards (MDLs), ability to perform in complex matrices, robotics capability, remote capabilities (2), modem cost savings, underwater capabilities (3) low cost savings
known program drivers: regulatory, non-proliferation, high
other comments: incorporates 2. remote as performance spec. 3. as a special application (low cost savings) underwater

need: detecting individual radioactive metal in asbestos
current state: physical sampling, alpha and beta counters
key performance char.: same as 1+volumetric analysis, speciation, isotope id, MDLs below (?) release level, must operate in complex matrices and mixtures, remote
known program drivers: cost savings: medium

need: detecting RCRA metals in concrete, metal, other solids
current state: XRF, sampling and analysis, immunoassay (surface?) for Hg.
key performance drivers: speciation (Cr^3 Cr^6), phase (Hg volatile) specific characterization, id of some chemical form, detection level < action level, remote operation
known program drivers: EPA/State, cost savings: Medium (DOE)/High (Outside)
other comments: incorporates -- remote pen. CA/AR (?)

need: detecting RCRA metals in asbestos
current state: same as #5 (in table above) XRF, sampling and analysis
key performance char.: same as #5 (in table above) with volumetric analysis
known program drivers: same as #5. cost savings -- same as #5.

Comments on Needs

Radiation Detection Needs

DOE

Utilities (include international) cost savings roughly equal medium to high for DOE.

Baseline technologies:

- Sample and lab analysis
- gross counters

Det. rads in asbestos.

Det. level has to be low enough to support “leave or remove” asbestos only decision.

Metals

Plating industry

Group 4: Air Quality Monitoring

Reported by Stephan Weeks

Needs Ranking

Priority	Need
1	Representative Sampling
2	Point Source Characterization of HAPS (189)
3	Near Real-time Monitoring of HAPS for Point Sources
4	Boundary Monitoring of HAPS
5	Broad Area/ Mobile Source Characterization of HAPS
6	Broad Area/ Mobile Source Monitoring of HAPS
7	Boundary Characterization of HAPS
8	Remote Sensing
9	Indoor/ Workplace Characterization and Monitoring
10	Aerial Measurements
11	Stratispheric Measurements
12	HAZWRAP Emergency Response
13	"Terrorism" monitors and Emergency response
15	Battlefield Sensors

Baseline technology:

Canister samples collection, transport to lab, lab analysis by approved methods.

Other technologies:

FTIR, NIR, portable GC, portable GC/MS, Ion Mobility (IMS), SAW, UV, LIF, Laser DIAL, X-RAY, DOAS (uv); AA, ICP-AES, ICP-MS, electrochemical diode FM, Raman, LSS, LIBS

Hazardous Air Pollutants (HAPS)

organic	particulates	metals	small inorganic
VOC		RCRA	O3
HC		Toxic	NOx
CH4		Hg	SOx
(combustion products)			Hz
PACs			NH_3
CFCs			CN
halocarbons			
smoke/haze			

Detecting: ⇒ ID and quantity ⇒ characterization, multicomponent

Monitoring: ⇒ detection on periodic basis of limited set of components, also assess total amount

Key Performance Characteristics:

on site

deployable includes ruggedness and portability

near real-time; < 30 minutes

reliability; operate > 6 months without service
ease of use; operated by nonprofessional
detect at required level e.g. 1 ppb
calibration/accuracy (about 20%)/ self-calibrating
sample collection
analyte preconcentration
provide process control data
selectivity/specificity e.g. congener
non-intrusive in situ vs. extractive
conveniently wearable
measure heterogeneous sample

Continuous Emission Monitoring with Instantaneous Permitting

Drivers

EPA, CAA, compliance monitoring and permitting
state regulations
DOD nonproliferation
DOE
OSHA
Worker Compensation
Legal Suits
Industry-specific rules for HAPs

Cost saving

e.g. facility perimeter monitoring with FTIR saves $15M over 15 years vs. canister sampling

Other comments

Do industry by industry assessment
Industrial liability if characterization done

Needs Descriptions

need: representative sampling
current state: canister: in situ, grab bag, extractive Isokinetic, preconcentrators, filter, baseline, state-of -the-art??
key performance char.: representative, concentrates analyte -- meet detectability requirements e.g. 1 ppb
known program drivers: EPA, CAA

need: real time/near-real time monitoring of hazardous air pollutants
current state: sample collection on site transportation to lab and analysis via approved techniques
key performance char.: development of instruments capable of operating on site
1. sample collection/concentration
2. analysis on site
3. data interpretation on site (or remote but results available on site for)

known program drivers: develop information which will be incorporated into process improving process efficiency product quality, environmental quality -- reduction in complexity of regulatory process permitting , etc.

need: perimeter monitoring of facilities to furnish near real-time results for HAPs, compliance under the CAA of 1990 as well as to provide an emergency response to protect the health and safety of neighboring communities

current state: present canister methods are too slow and expensive. FTIR systems are just being applied and have potential to fill this need.

key performance char.: long-term instrument reliability needs to be demonstrated. the instrument should operate reliably over > 6 months period without maintenance and have an MTBF > 2 years. operation by non-professional is required.

known program drivers: JD Tate of Dow Chemical has made a comparison of an FTIR System with a canister systems showing a $15 million saving over a 15 year period. The initial higher capital cost of the FTIR becomes more economical over the high labor cost of canister methods over a multi-year period.

need: identify, quantify any/each of 189 HAPs at property line of industrial operation to measure compliance with Clean Air Act II within 30 minutes.

current state: 1) portable GC 2) portable GC/MS 3) FTIR/open path 4) analytic-specific sensor/monitor

key performance char.: 1) identify HAPs contaminant in presence of congener, 2) quantity HAPs in congener matrix 3) detect requisite level (ca. 1 ppb) of any/each HAPs, 4) accuracy within 20% in presence of congener 5) result available in 30 minutes

known program drivers: 1) EPA enforcement of Clean Air Act 2) industry-specific rules for HAPS which are present in specific industries 3) state response to Clean Air Act

need: monitor any/each of 600 OSHA-regulated air contaminants in breathing zone of workers in compliance we with OSHA Ace of 1970

current state: 1) pump sampling with charcoal, silica, etc. tub (analysis of sample in lab) 2) diffusive monitors/samplers (analysis of sample in lab) 3) portable-wearable real-time instrument

key performance char.: 1) monitor accuracy (95% confidence, about 25% of the value) in presence of congeners 2) non-intrusive 3) conveniently wearable 4) results in timely manner a. 10 minutes b. one hour c. one day d. one month

known program drivers: 1) OSHA compliance policy 2) workers comp. claims from employees 3) liability from suits by suits from non-employees

need: near real-time monitoring of HAPS

current state: surface acoustic waves (SAW), ion mobility spectroscopy

key performance char.: sample preparation (limited detection), self calibration, reliability, ruggedness

need: compliance assurance monitoring

current state: sample collection, transport, lab analysis, canister methods

key performance char.: reliable data, CAM instantaneous permitting, compliance assurance monitoring, near real-time, reliability, ruggedness, portability, deployable, calibration - accuracy, no service > 6 months, ease of use, non professional operation

known program drivers: CAA

other comments: emergency response

need: In view of the need for real-time, in situ, and portable systems, its seems to me that the need for “traditional” spectroscopic techniques should be less utilized. Instead novel mechanisms of sensing either specific species or an array of species is where to look for solutions.

current state: These detection systems are usually more easily adapted to portable instrumentation.

Discussion Comments

Remote sensing (e.g. via FTIR) has application in PP and containment areas (industrial processing (leaks)) (William Walter, AIL)

indoor and workplace monitoring should be rated as a high priority due to many D&D activities (Mitch Erickson)

GROUP 5: EFFLUENTS MONITORING

Reported by Richard Ediger

Needs ranking

The workgroup considered the seven needs suggested to them, added an eighth need, and ranked them. The table on the following page contains rankings, baseline technologies, and comments on these needs.

The discussion leader made the following additional points:

> Applications include pollution prevention and containment in many industries
>
> Most sensors are responsive to only a few analytes, but effluent monitoring may in some cases require detection of many analytes.
>
> Regulations will drive both what analytes must be detected and the commercial market for instrumentation to monitor those analytes.
>
> Some of the key analytes that may need to be monitored in the inorganic category include nitrogenous ions such as cyanide.
>
> Considerably better definitions of needs are required before commercial investment can be justified.

Discussion summary

The top four or five needs (in the table on the following page) appear to be most significant and have overlap between DOE and commercial needs.

Monitoring of organics may not require detection of specific compounds in many cases. There are 30,000 permit holders in the US who must monitor for organics or RCRA metals. A common baseline general organic monitoring technology is freon extraction followed by infrared analysis of the extract.

For a large company, approximately \$50M in sales over 5 yr is required to justify a \$5M investment in a new instrument.

The monitoring of effluent for radioactive components should be considered a DOER need of high significance.

APPENDIX B

EFFLUENTS MONITORING NEEDS

Rank	Need	Baseline	Key Performance Characteristics	Implementable	Comments
1	Analyzing individual organics in water/liquids	GC, GC-MS, Immunoassay HPLC, Raman, FTIR, UV, Fluorescence	Safety, Mobilization Potential, Sample Size Minimization, EPA Levels (Regulatory), Matrix Effects, Durability		
2	Analyzing individual RCRA metals in water	Cold Vapor AA (Hg), ICP-AES and MS, "Jerome Instrument"	Same as above		
3	Analyzing inorganics and other contaminants in water	UV/Vis, titration, colorimetry, Chemical Sensors	Same as above		No real regulatory driver, include pH, specifically CN, sulfide, NOx_1 SOx
4	Analyzing organics in stack emissions	FTIR, GC, Fast GC, SAWs	Same as above		No real regulatory drivers
5	Analyzing inorganics in stack emissions	IR, GC, NIR, Chemiluminescence	Same as above		No real regulatory drivers, H_2S, NOx_1, NH_3, Cl_2, SOx, etc
6	Analyzing metals in stack emissions	LIBS (unproved), Hg analyzers, AA, XRF	Same as above		No real regulatory drivers
7	Analyzing individual radioactive metals in water	ICP-AES or MS; Chem Lum (U)	Same as above	Not very relevant	Needs to be generic. They can vary drastically with sample complexity
8	Analyzing minor radioactive constituents in solution with high transuranics	ICP-MS, phosphori-metry	Same as above	Little Savings potential	For effluents monitoring, needs tend toward municipal or industrial over DOE requirements

GROUP 6: PROCESS MONITORS AND CONTROL/ RESOURCE RECOVERY

Reported by Diana Blair

Needs ranking

- Highest priority **Technology Development**
  - inlet characterization
  - effluent monitoring
- DOE specific needs
  - radioactive materials in mixed, condensed phase
  - organics/RCRA metals in water
- BROADER MARKET (primarily niche markets)
  - organics in water
  - metals in water
  - auto emissions

PC&M Performance Characterization

- reliability
- ease of maintenance
- relative low cost (long term usage will offset costs)
- simple (mask complexity)
- sampling interface

Process control

- Defined process
- Drivers: not regulatory, Economic.

Discussion summary

Sensors are needed for multiple phase streams:

mass/phase
part size distribution
bubble size distribution
viscosity

Broader market size is estimated to be approximately 1m to 1000M. Market is collection of many small niche markets.

Cost savings of up to 45% can be achieved in some cases (Jim Butler)

GROUP 7: WASTE CHARACTERIZATION

Reported by Bryce Smith

Needs ranking

High Priority Needs

- Detecting individual radioactive metals in sludge.
- Detecting radioactive metals in waste drums and boxes non-destructively.
- Detecting individual radioactivities in high level waste tanks in-situ.
- Detecting RCRA metals in waste drums and boxes non-destructively
- Detecting individual organics (inorganics) in air in-situ (i.e. tank headspace)

Medium Priority Needs

- Detecting individual RCRA metals in sludge.
- Detecting physical properties of high level waste in tanks.
- Detecting organics in wastes drums and boxes non-destructively.

Low Priority Needs

- Detecting radiological properties.
  3D mapped in field
- Detecting chemical properties.
  3D mapped in field
- Detecting individual organics in sludge.
- Detecting TOC content in Tank waste
- Detecting general contaminants in drums and boxes in-situ.

Discussion summary

Detection of inorganics in UST salt cake is required for process inlet characterization. One cannot retrieve waste prior to such characterization. (Phong)

Market for tank waster characterization can be judged from fact that there are 300 tanks in DOE and 600 tanks in world. (Gilchrist)

Better description of needs will be available soon from Tanks focus area.

Consider funding tailoring of existing technology to DOE needs. (Edwards)

Disseminate specific information re needs. (Edwards)

Fire departments often need to know contents of organics in drums at a fire scene. (Portnoff)